Synthesis and Characterization of Triaminocyclopropenium Ionic Liquids

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Abstract

This thesis describes the synthesis and characterization of triaminocyclopropenium, $[C_3(NR_2)_3]^+$, ionic liquids. A range of triaminocyclopropenium salts were prepared: D_{3h}, C_{3h}, C_{2v} and C_s symmetric cations with a variety of substituents. D_{3h} and C_{3h} symmetric cations were prepared from pentachlorocyclopropane and dialkylamines, whereas a variety of methods were investigated for C_{2v} and C_s symmetric cations, with the most versatile synthesis involving the alkylation of bis(dialkylamino)cyclopropenone followed by reaction with dialkylamine. Metathesis with a range of common ionic liquid anions was carried out to facilitate comparisons to other common classes of ionic liquids.

The triaminocyclopropenium salts were characterized by standard techniques (^{1}H-, ^{13}C{^{1}H}-NMR, ES$^+$ MS, microanalysis) as well as particular physicochemical properties relevant to ionic liquids. The thermal behaviour was examined with DSC, with the majority of salts being liquid at room temperature. The viscosity of triaminocyclopropenium ionic liquids was similar to other classes of ionic liquid cations, in the range of 58.4 to 554 mPa s at 20 °C. This is despite the generally large size of the cations investigated, which also causes the conductivity to be lower. Triaminocyclopropenium ionic liquids show good ionicity, more than other common classes of ionic liquid cation, which is likely due to the relatively electron-rich nature of the cation. The thermal, electrochemical and chemical stability of triaminocyclopropenium ionic liquids was accessed. Good thermal stabilities were observed, with onset temperatures of 339 to 413 °C. The electrochemical window of $[C_3(NEt_2)_3]$TFSA is 3.6 V, this is low due to the easy oxidation of the cation. The chemical stability is good under acidic, weakly-basic, weakly-nucleophilic, reducing and weakly-oxidising conditions, however, the cations are unstable to the strong nucleophile/base hydroxide. Triaminocyclopropenium ionic liquids showed a full range of solubility and miscibility: from fully miscible in water to fully miscible in hexane.

A preliminary investigation of ionic liquid fluorides was carried out. While stable ionic liquids with naked fluorides were not obtained, ionic liquids with strongly-bound solvate

molecules (ethanol and acetic acid) were seeen, and their viscosity, conductivity and density were measured. The attachment of hydroxyl functional groups to triaminocyclopropenium cations was seen to improve the stability of ionic liquid fluorides, although at the cost of high viscosity.

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List of Abbreviations

TFSA	Bis(trifluoromethanesulfonyl)amide
DCA	Dicyanamide
OTf	Trifluoromethanesulfonate
DBP	Dibutylphosphate
Me	Methyl, CH_3-
Et	Ethyl, CH_3CH_2-
Pr	n-Propyl, $CH_3CH_2CH_2$-
^{i}Pr	iso-Propyl, $(CH_3)_2CH$-
Bu	n-Butyl, $CH_3(CH_2)_2CH_2$-
Pent	n-Pentyl, $CH_3(CH_2)_3CH_2$-
Hex	n-Hexyl, $CH_3(CH_2)_4CH_2$-
Dec	n-Decyl $CH_3(CH_2)_8CH_2$-
$[C_nMIM]^+$	1-alkyl-3-methylimidazolium, alkyl length of n
$[P_{14,6,6,6}]^+$	trihexyltetradecylphosphonium
$[N_{6,2,2,2}]^+$	Triethylhexylammonium
$[C_4py]^+$	1-butylpyridinium
$[C_4Mpy]^+$	1-butyl-3-methylpyridinium
$[p_{1,4}]^+$	Butylmethylpyrrolidinium

Chapter 1

1 Introduction

In recent years, interest in ionic liquids (ILs) has grown due to a number of interesting properties that these liquids can exhibit. While the potential number of ionic liquids is huge, estimated at 10^6,[1] the current range of ionic liquids is based on a few main classes of ions. This research has investigated ionic liquids with the triaminocyclopropenium cation, looking at the synthesis and then the properties of this novel class of ionic liquids.

1.1 Ionic liquids

The common definition of an ionic liquid is that it is a compound composed entirely of ions and has a melting point of less than 100 °C.[2-5] However, this is a very loose definition for two reasons: firstly, 100 °C is only an arbitrary number and secondly, mixtures of ionic liquids with ionic salts, molecular solvents or other compounds can also be of interest.[6] Of particular interest are ionic liquids that melt below room temperature; these are often referred to as room temperature ionic liquids (RTILs).

1.1.1 Ions used in ionic liquids

Ionic liquids are generally composed of an organic cation with an inorganic anion. The combination of different anions and cations creates a huge number of potential ionic liquids, and this number just increases exponentially when mixtures of ionic liquids are also considered. Ionic liquids can be classified as either aprotic or protic ionic liquids, with aprotic ionic liquids being permanently charged, while protic ionic liquids[7-9] are in an equilibrium between a protonated cation and the conjugate acid of the anion, with the ionized side dominating (Equation 1). The triaminocyclopropenium cation is usually aprotic, and the discussion will reflect that.

$$HA + B \rightleftharpoons BH^+ + A^-$$

Equation 1 – Equilibrium between neutral and ionized species in protic ionic liquids

There are currently four main classes of cations (Figure 1.1): 1,3-dialkylimidazolium,[10-13] 1-alkylpyridinium,[14] tetraalkyl-ammonium[15] and -phosphonium.[16,17] 1,3-dialkylimidazolium is the most commonly used ionic liquid cation, particularly 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium, as this class of cation gives low melting points and low viscosities (for an ionic liquid). 1,3-dialkylimidazolium and 1-alkylpyridinium are both aromatic cations. Due to this, the protons on the ring have higher acidicity than on alkyl chains, especially the proton at the 2 position of 1,3-dialkylimidazolium cations, and this can play a role in the properties of these ionic liquids. Tetraalkyl-ammonium and –phosphonium are both quaternary cations, and because of the concentrated charge, long chains of various lengths are usually required to lower melting points, resulting in viscous liquids.

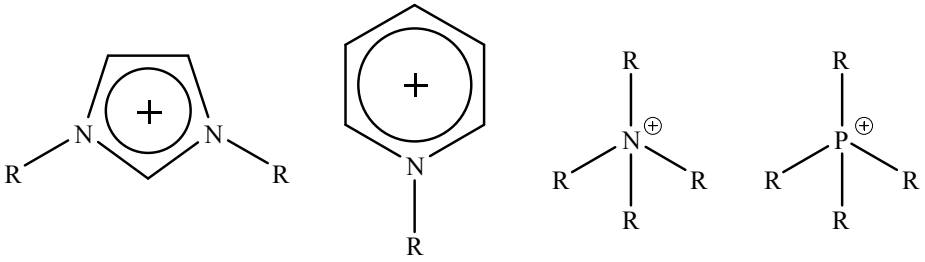


Figure 1.1 – Main classes of ionic liquid cation: 1,3-dialkylimidazolium, alkylpyridinium, tetraalkyl-ammonium and –phosphonium

There are also other classes, such as pyrazolium, pyrrolinium, sulfonium and guanidinium. Guanidinium[18-24] (Figure 1.2) is noteworthy in context of this work because of the similarity to triaminocyclopropenium: a central cation is stabilized by three surrounding nitrogen substituents.

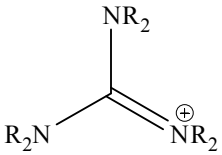


Figure 1.2 – Hexalkylguanidinium cation

Ionic liquids often use an inorganic anion as these often give desirable liquid properties, although organic anions are also used. A range of common ionic liquid anions[2,25,26] are

shown below (Figure 1.3). All shown here carry a single negative charge, most are polyatomic and have a dispersed charge, either via delocalisation or strongly electron-withdrawing substituents.

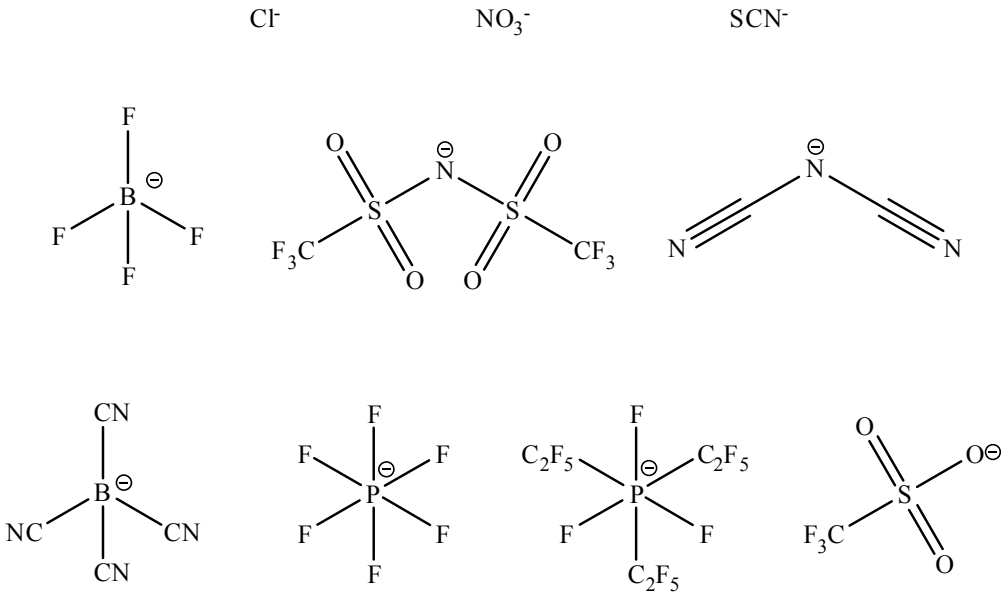


Figure 1.3 – Common ionic liquid anions. From top left: chloride, nitrate, thiocyanate, BF_4, TFSA, DCA, tetracyanoborate, hexafluorophosphate, tris(pentafluoroethyl)trifluorophosphate, OTf

1.1.2 Properties of ionic liquids

Ionic liquids can have a wide range of properties. They have been described as "designer solvents", because the ability to vary the ions (either by changing class or substituents) means particular properties can be tuned as desired. Some of the properties that are of interest will be discussed in the following paragraphs. This section contains a brief discussion as more extensive description is given in the relevant section for each investigated property.

Many aprotic ionic liquids have very low or negligible vapor pressure, and therefore do not evaporate. Despite what was once thought, aprotic ionic liquids do have a vapor pressure and some can be distilled. However, in many cases this requires temperatures of 200-300 °C, and low pressure, about 5 mbar. Even under these conditions, some ionic liquids will not vaporize below their decomposition temperature.[27] In the case of aprotic

ionic liquids, the low vapor pressure is due to the need to vaporize the ionic liquid as a neutral ion pair,[28] as it is not favorable for ions to overcome the cohesive forces. Protic ionic liquids, on the other hand, are often easily distillable, due to the neutral species present in the equilibrium. The low vapor pressure of ionic liquids is a useful property industrially, and ionic liquids show potential to replace some volatile organic compounds (VOCs) in industrial applications.[29] This may have environmental and safety benefits.

Ionic liquids have good thermal stability, with onset decomposition temperatures up to 400 °C,[30-34] although this is dependent on the conditions and quality of the sample. The onset temperatures are an overestimation of the thermal stability, however, many ionic liquids can still be used at temperatures of over 200 °C.

The lack of a boiling point, coupled with a good thermal stability, means that ionic liquids have a wide liquid range of up to 300 °C. This is a potentially useful property as it means the temperature of a reaction or process can be controlled over a wide range without changing solvent.

Ionic liquids can be non flammable, which is helped by the good thermal stability and low volatility. On the other hand, hypergolic ionic liquids have also been made,[35,36] which demonstrates the range of properties that ionic liquids can have.

Ionic liquids can dissolve a range of compounds[37-44] – organic, inorganic, organometallic, gases, liquids or solids. Even some hard to dissolve biomolecules such as cellulose are soluble in some ionic liquids.[45-47] The polarity, polarisability and specific interactions can be tuned to suit a particular solute. Many different reactions can be carried out in ionic liquids, and the different solvent environments of ionic liquids can be used to influence the course of the reaction.[48]

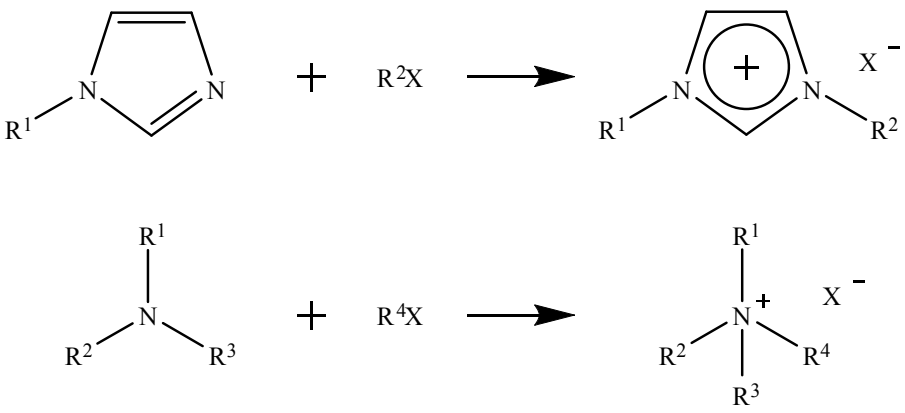
Ionic liquids are conductive, since they are composed of mobile ions. Conductivity is generally lower[2,49-51] than aqueous electrolytes because of the higher viscosity, however, this is not necessarily an impassable problem. Ionic liquids can also have a large

electrochemical window, up to 6V, allowing many electrochemical reactions to be done in them without degrading the solvent. Ionic liquids have found use in applications such as battery electrolytes and electrochemical processing of metal surfaces.

1.1.3 Synthesis of ionic liquids

The synthesis of ionic liquids has been an important aspect of the development of the field. Improvements in the synthesis of ionic liquids has meant these liquids have gone from coloured liquids with high levels of impurities, such as halides and water, to colourless liquids with a high purity, and at a lower cost. The synthesis of protic ionic liquids almost always involves the mixing of the respective acid and base. An example of this is the first published ionic liquid,[29] ethylammonium nitrate, which is synthesized by addition of nitric acid to a cooled solution of ethylamine.

Aprotic ionic liquids generally involve a quarternization reaction, using an alkylating reagent to form the permanent cation.[52] Two examples are shown, the synthesis of 1,3-dialkylimidazolium and tetraalkylammonium cations (Scheme 1) from 1-alkylimidazole and trialkylamine, respectively, which is the usual method. A wide variety of alkylating agents can be used: haloalkanes, dialkylsulfates, alkyltriflates, alkyltrifluoroacetates or alkyl tosylates. The conditions of the reaction will depend on the reactivity of the alkylating agent; for example, chloroalkanes require heating for extended periods of time, but iodoalkanes require less time. Autoclaves have often been employed with the more volatile alkylating agents such as chloroethane. The choice of alkylating agent is often determined by the intended use of the ionic liquid, with alkylating agents that produce anions with favourable properties not requiring another anion exchange step being desirable. The haloalkane alkylating agents are still common due to halide anions being easily exchanged to the widest variety of anions.



Scheme 1 – Synthesis of 1,3-dialkylimidazolium and tetraalkylammonium cations

Other methods for the synthesis of these ionic liquids are published in the literature, however, those methods are not discussed here as they are outside the scope of this work.

The purification of ionic liquids is also an important aspect.[53-56] During the synthesis of ionic liquids, it is usual to use high purity starting materials, as the removal of impurities later can be difficult. Due to the low volatility of ionic liquids, distillation is generally not possible, however, this means that any volatile starting materials can be removed, often under reduced pressure, without losing any product. For ionic liquids with melting points above ambient temperature, recrystallisation can be carried out.

1.2 Triaminocyclopropenium cations

1.2.1 Structure of triaminocyclopropenium cations

The first cyclopropenium cation to be reported was triphenylcyclopropenium, synthesized by Breslow in 1957,[57] although the stability of this was not good and it decomposed slowly in alcohols. Later, in 1962, the tris(isopropyl)cyclopropenium cation was synthesized, and this has improved stability compared to the triphenylcyclopropenium.[58] This indicates that the electron-donating σ-inductive effect of the propyl group is greater than the electron-donating π-conjugative effect of the phenyl group, which is confirmed by HMO and INDO calculations.[59,60] Several reviews of cyclopropenium chemistry are available.[59,61,62]

The first triaminocyclopropenium cation, tris(dimethylamino)cyclopropenium $[C_3(NMe_2)_3]^+$ (Figure 1.4), was synthesized by Yoshida in 1971.[63] This is seen to have much higher stability, even stable in water at 100 °C, which is due to the amino substituents. Nitrogen is of course an electron-withdrawing σ-inductive atom, but this is less than its electron-donating π-conjugative effect, as shown by the HMO and INDO calculations.[59,60] Triaminocyclopropenium has more electron density on the ring carbons compared to $[C_3H_3]^+$ by 0.17 electrons per carbon, and a partial positive charge on the nitrogen. This is also reflected in a lower bond order of the π bond between ring carbons, 0.570 for triaminocyclopropenium compared to 0.667 for $[C_3H_3]^+$, and an exocyclic C-N π bond order of 0.453, with a calculated barrier to rotation of 58.1 kJmol^{-1}.

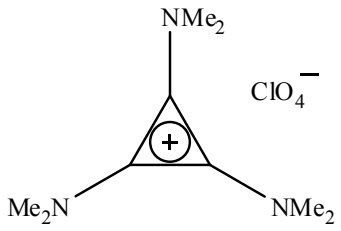


Figure 1.4 – Tris(dimethylamino)cyclopropenium perchlorate, $[C_3(NMe_2)_3]ClO_4$

The crystal structure of $[C_3(NMe_2)_3]ClO_4$ was reported in 1971,[64] this shows a shorter C-C bond of 1.363 Å than in benzene (1.398 Å), which is consistent with cyclopropenium having bent sigma bonds. The exocyclic C-N bonds are 1.333 Å, which is in between C-N single bonds (1.47 Å) and C-N double bonds (1.29 Å), this is consistent with π donation from the p orbital of the nitrogen back into the ring. The N-Me bond length is slightly shorter than normal (1.47 Å), which is consistent with resonance delocalizing partial positive charge onto the nitrogen. The cation is not quite planar, with two nitrogen substituents bending one way, and all methyl groups are also bending one way, although later IR experiments show this is not important in solution, and the structure can be approximated to D_{3h} symmetry. The plane of N-Me_2 is twisted compared to the cyclopropenium ring (20.8° and 9.9°), which decreases hydrogen-hydrogen interactions, but the nitrogen is still sp^2 hybridized, showing that the nitrogen is involved in π donation.

There have been a number of crystal structures reported, although most are $[C_3(NMe_2)_3]^+$ with various anions, and all have relatively inflexible substituents. Crystal structures have been reported for $[C_3(NMe_2)_3]^+$ with ClO_4^-,[64] $[Pt_2Cl_6]^{2-}$,[65,66] tetracyanoquinodimethanide, [67]2,3-dichloro-5,6-dicyanobenzoquinonide,[68] $[NbOCl_4.H_2O]^-$,[69] $[NbCl_6]^-$ and $[TaCl_6]^-$,[70] $[SbCl_6]^-$[71] and I_3^-.[72] Structures of a few other triaminocyclopropenium salts have also been reported: $[C_3(NC_5H_{10})_3]ClO_4$[73] $[C_3(N^iPr_2)_3]ClO_4$ and $[C_3(N^iPr_2)_2NMe_2]ClO_4$.[74,75] A bis(dialkylamino)chlorocyclopropenium cation structure has also been reported, $[C_3(N^iPr_2)_2Cl]Cl$.[73]

The only exception in the literature to the nitrogen substituent being planar is $[C_3(N^iPr_2)_3]^+$ [74,75], where the steric hindrance of the bulky isopropyl groups prevents all three diisopropylamino substituents from being planar. In this case, one of the nitrogen substituents gains more sp^3 character, and one of its ^{i}Pr-N bonds is perpendicular to the plane of the ring.

Krebs and Breckwoldt[76] have reported experimentally measured barriers to the exocyclic C-N bond rotation of $\Delta G^‡$ = 95–105 kJ mol^{-1} for monoaminocyclopropeniums $[C_3X_2NR_2]^+$ (where X = Me or Ph and R = Me or aryl) and Clark[73] reported a barrier of $\Delta G^‡$ = 75 kJ mol^{-1} for the diamino-substituted cation $[C_3(N^iPr_2)_2Cl]^+$. A lower barrier to rotation for triaminocyclopropenium cations can be expected due to three competing amino substituents reducing donation from each.

Cyclopropenium is a highly-strained system, and this has important effects on the hybridization of the ring carbons.[77] The exocyclic bond is approximately sp hybridized, while the ring bonds are sp^3, instead of sp^2 for a normal tricoordinate carbon. This is because of high ring strain causing more p character in the ring sigma bonds, which lessens the ring strain (as the ideal angle between bonds drops from 120 to 109°). Even with this lowering of the angle, it is still necessary for the σ bonds to be bent bonds, as the internal 60° angle is not possible.

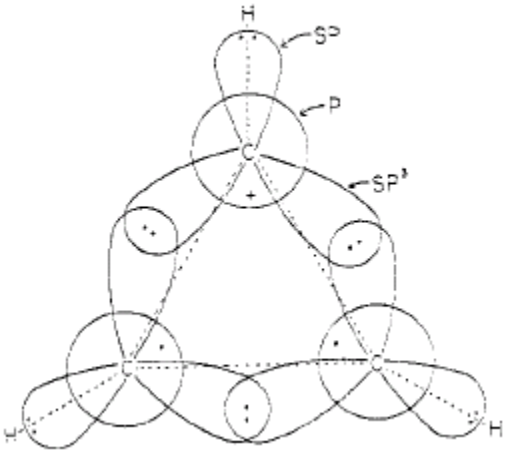


Figure 1.5 – Orbitals of cyclopropenium[77]

The π molecular orbitals are important to consider. The MO diagram[78,79] (Figure 1.6) uses the cyclopropenium π orbitals, and combines them with group orbitals from the substituent nitrogen p orbitals. The HOMO orbital is a combination of the C_3 and the nitrogen ligands symmetric group orbitals in an antibonding fashion, and is thus quite a high energy HOMO orbital.

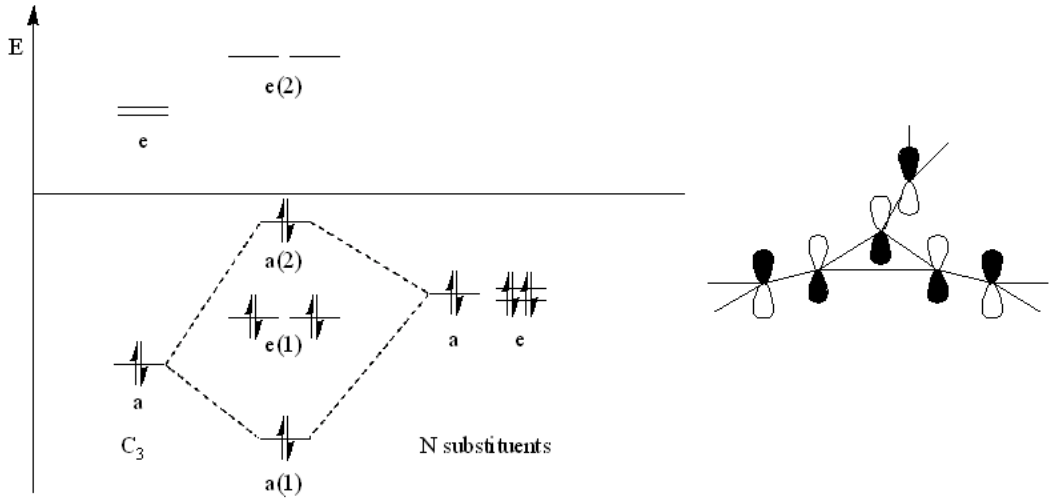


Figure 1.6 – Molecular orbital diagram of π orbitals and HOMO of triaminocyclopropenium

1.2.2 Properties of triaminocyclopropenium salts

This section will review the known properties of triaminocyclopropenium salts. Yoshida[59,63,79-88] was the first to synthesize and describe a triaminocyclopropenium salt. He found, in terms of properties, that triaminocyclopropenium perchlorate salts are soluble in polar organic solvents, stable in the atmosphere and not hygroscopic. They are even stable in water at 100 °C, as opposed to trichloro- and triphenyl-cyclopropenium cations. The melting points were reported for $[C_3(NC_5H_5)_3]ClO_4$ and $[C_3(NC_4H_4O)_3]ClO_4$, however, due to the symmetric and inflexible side chains used and the perchlorate anion, the melting points are high, 146 and 270 °C (decomposition), respectively. Later, Wilcox[89] prepared $[C_3(NEt_2)_3]ClO_4$ and reported a melting point of 37.5 – 38.5 °C, which is possibily the first reported triaminocyclopropenium ionic liquid.

UV/Vis spectrometry in MeOH of $[C_3(NMe_2)_3]ClO_4$ showed an absorption at 233 nm (ε = 16600), which is assigned to an intra-molecular charge transfer band from the amino group to the cyclopropenium ring. All aminocyclopropeniums have at least one peak in the range 206-312 nm. INDO calculations determine this to be a charge transfer from the amino group into the cyclopropenium.

Kerber[90] looked at the thermodynamic stability of substituted bis(phenyl)cyclopropenium, $[C_3Ph_2R]^+$. This is done by looking at the pK_{R+} value, which is the pH necessary to establish a 1:1 equilibrium between the diphenylcyclopropenium and the derived alcohol.[58,77] The more stable a cation is, the more it resists hydroxide attack, the higher the pH needs to be to establish a 1:1 ratio.

$$[C_3Ph_2R]^+ + OH^- \overset{K_{R+}}{\rightleftharpoons} C_3Ph_2ROH$$

Scheme 2 – Stability determination of bis(phenyl)cyclopropenium cations

Various substituents on bis(phenyl)cyclopropenium were used, and the results showed that cyclopropenium salts with dialkylamino substituents are much more stable than with carbon (alkyl and phenyl), oxygen (alkoxy), sulfur (alkythio) or hydrogen substituents.

The bis(phenyl)dialkylaminocyclopropenium salt has a pK_{R+} of >10, while with the other substituents, pK_{R+} ranged from -0.7 to 5. Yoshida attempted similar work with triaminocyclopropenium salts in order to find pK_{R+},[86,87] however, the potentiometric titration method was not successful. Yoshida did report an empirical correlation between known pK_{R+} values and the position of the ring deformation infra red peak of cyclopropenium ions (~1300-1500 cm^{-1}). Using this correlation pK_{R+} values for triaminocyclopropenium were estimated to be approximately 13. The correlation is due the various substituents affecting both the stability and the ring bonding, and thus the position of the infra red peak.

Yoshida[87] and Clark[73] have taken infra red and Raman spectra of triaminocyclopropenium salts, and assigned their peaks to the various vibrations. Characteristic symmetric (~1900 cm^{-1}) and asymmetric (~1500 cm^{-1}) vibrations of the cyclopropenium ring are observed.

Yoshida, Gerson and Plattner investigated the electrochemical behaviour of $[C_3(NMe_2)_3]^+$.[79] While they were not able to reduce the cation, it was able to be oxidized with concentrated sulfuric acid or electrochemically. They reported and analyzed the Electron Paramagnetic Resonance (EPR) spectrum of the resulting dication radical. Through Hückel molecular orbital calculations, they show that the LUMO is relatively high and therefore hard to reduce, and the HOMO is relatively high and therefore easy to oxidize – as was seen on the molecular orbital diagram in the previous section. Later, Weiss[91] was able to isolate triaminocyclopropenium radical dications via reaction with antimony pentachloride ($SbCl_5$), which were stable in the atmosphere for several hours.

The electrochemistry of triaminocyclopropenium was examined in acetonitrile solutions,[92] which showed that $[C_3(NMe_2)_3]^+$ is oxidized at +1.3V vs NHE to a dication radical, and then again at +2.3 V to a trication. It is interesting to note that this is relatively low, similar to the oxidiation of Cl^-, because of the high-lying HOMO. This first oxidation is about 1.6 V lower than for trimethylcyclopropenium or triphenylcyclopropenium substituents, and 1.2 V lower than

tris(thioethoxy)cyclopropenium. This is due to triaminocyclopropenium being electron rich compared to the other cyclopropeniums. The electron rich nature of the triaminocyclopropenium cation is one of its noteworthy characteristics. Reduction of $[C_3(NMe_2)_3]^+$ was greater than –3.0 V, due to the LUMO being high energy. Reduction was higher for tris(thioethoxy)cyclopropenium (–1.4), trimethylcyclopropenium (–1.2 V) and triphenylcyclopropenium (–0.8 V) due to these being relatively electron poor .

Surman *et al.*[93] used pulse radiolysis to generate the radical dication in aqueous solutions from $[C_3(NEt_2)_3]^+$ and $[C_3(NC_5H_{10})_3]^+$, and reported the oxidation at 1.23 ± 0.04 and 1.20 ± 0.03 V vs NHE, respectively.

The idea that triaminocyclopropenium is an electron-rich system, as opposed to most cations that are electron deficient, was also hinted at when H/D^+ exchange on bis(dialkylamino)cyclopropenium, $[C_3(NR_2)_2H]^+$, was observed occurring via electrophilic aromatic substitution.[94]

Weiss has suggested that the electron rich nature of triaminocyclopropenium also creates ion pair strain.[78] While the anion and cation are electrostatically attracted towards each other, they both have relatively high-energy filled orbitals, which creates orbital repulsion (closed shell repulsion). As the distance between the ions is decreased, the electrostatic attraction increases, however, so does the repulsion between the filled orbitals (Figure 1.7).

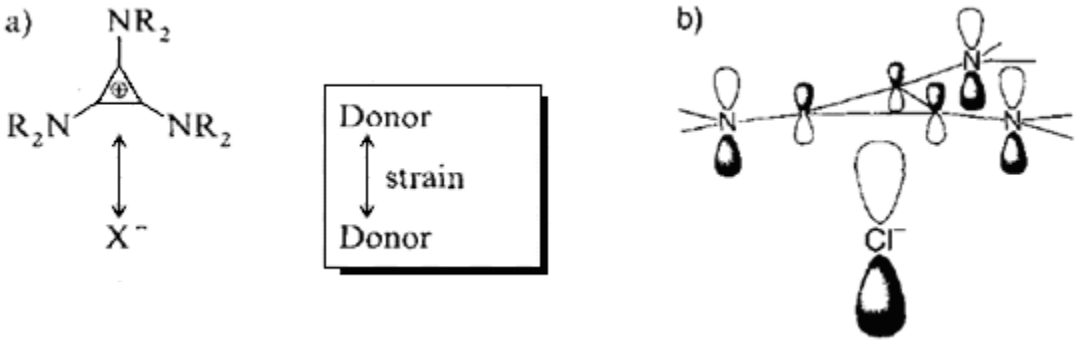


Figure 1.7 – Ion pair strain due to two electron rich species[95]

Weiss used this ion pair strain to create some novel anion systems that were not possible with other cation species.[78,95,96] Using $[C_3(NMe_2)_3]Cl$ and a variety of organic acids and phenols, 1:1 adducts were able to be precipitated. An X-Ray structure of the $[C_3(NMe_2)_3]Cl$ benzoic acid adduct showed a strong hydrogen bond between the chloride and acid, a hard-hard interaction. Other ammonium, guanidinium and phosphonium chloride salts were tried, however, no adducts were able to be isolated. To Weiss' knowledge, no other adducts of chloride and carboxylic acid which are connected by hydrogen bonds have been isolated. "The [ion pair strain] driving force of their formation must be considerable, as it requires the annulment of the classical low-energy association patterns of organic acids."

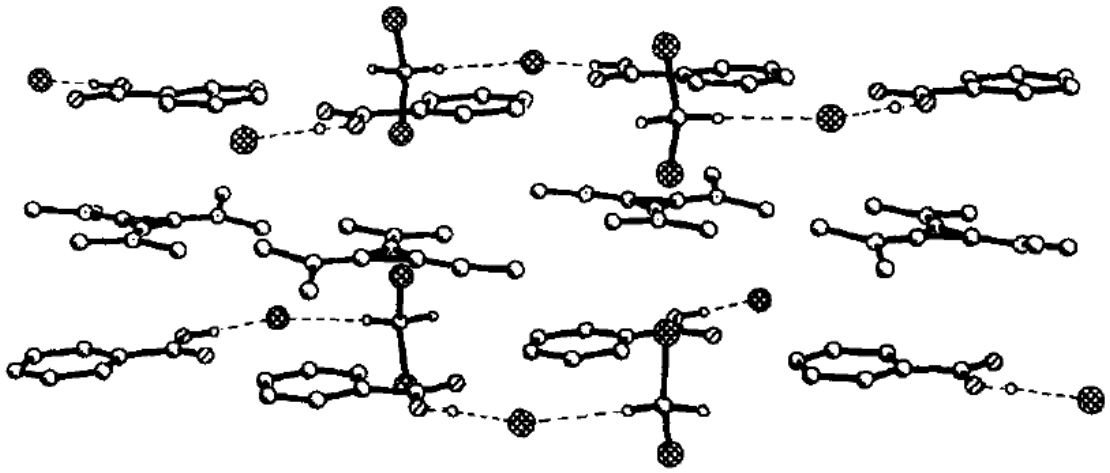


Figure 1.8 – Structure of $[C_3(NMe_2)_3]Cl$ and benzoic acid adduct[95]

The ion pair strain also drove the formation of unusual iodide adducts, soft-soft interactions.[96] $[C_3(NMe_2)_3]I$ salts were mixed with 2-iodo-1-phenylacetylene and diiodoacetylene, and formed crystal adducts with a 1:1 ratio. The iodoacetylenes are σ* acceptors, so form a weak bond with I^- which is an electron donor. The I-I distance is 3.44 Å, compared to sum of van der Waals radii of 4.35 Å.

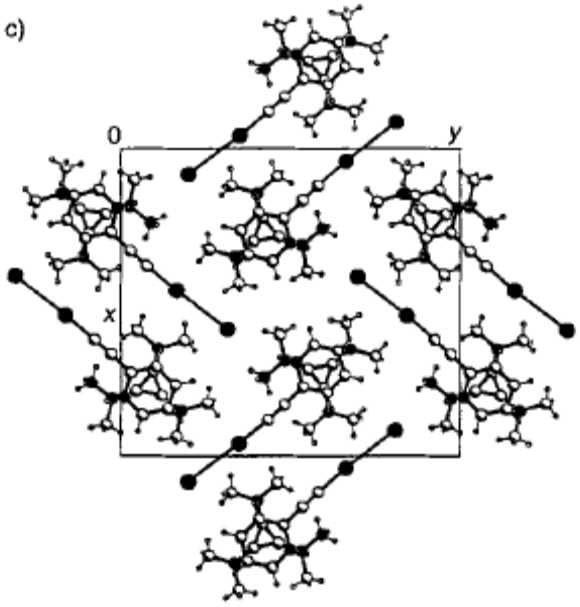


Figure 1.9 – Structure of $C_3(NMe_2)_3]I$ and 2-iodo-1-phenylacetylene adduct[96]

The ion pair strain is also thought to be a factor in the formation of a rare discrete dichloride cluster (Figure 1.10). In previous work from the Curnow group[75] the structure of $[C_3(N^iPr_2)_3]Cl.3H_2O$ was reported, with two chloride anions and water molecules existing in discrete cube rather than as the more common monochloride hydrates.

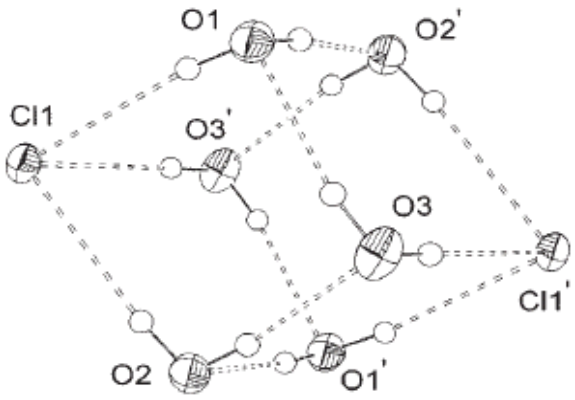
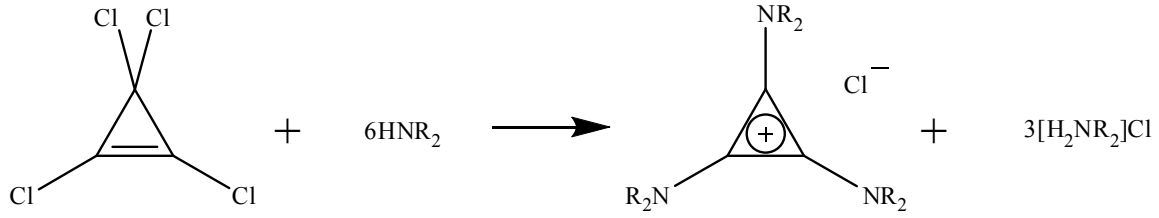


Figure 1.10 – Discrete dichloride hexahydrate cluster

1.2.3 Synthesis of triaminocyclopropenium salts

This section will review the syntheses of triaminocyclopropenium salts. Yoshida first synthesized these salts from tetrachlorocyclopropene (Scheme 3).[63] Excess dimethylamine, piperidine, morpholine, N-methylaniline and N-ethylaniline were added to tetrachlorocyclopropene at 0 °C, stirred for 5 h, then again at ambient temperature for 17 h, and then heated to reflux for 5 h. 70% perchloric acid was added, and the organic layer was extracted. However, when the synthesis of tris(diethylamino)cyclopropenium was attempted, for some unknown reason, the reaction stopped at chlorobis(diethylamino)cyclopropenium. In the NMR spectrum, two sets of peaks, very slightly offset, are observed for the two ethyl environments. Diisopropylamine also gives the di-substituted product, chlorobis(diisopropylamino)cyclopropenium, but this is due to steric hindrance preventing a third bulky amino group from adding to the ring. Other groups have also carried out this reaction between tetrachlorocyclopropene and diethylamine. Gompper *et al.*[97] got a yield of 15% of the chlorobis(diethylamino)cyclopropenium product, but could still spectroscopically identify tris(diethylamino)cyclopropenium in the product. Breslow,[89] in synthesizing bis(diethylamino)cyclopropenone, made the tris(diethylamino)cyclopropenone in good yield. Clark *et al.*[73] used Yoshida's method, but obtained only tris(diethylamino)cyclopropenium.



Scheme 3 – Synthesis of triaminocyclopropenium chloride from tetrachlorocyclopropene

In 1973, Yoshida proposed a mechanism[59] (Figure 1.11) in which an amine nucleophile attacks a ring vinylic carbon atom, which then pushes a chlorine substituent off the neighbouring carbon helped by excess dialkyl amine. This process is repeated twice more and then the last chlorine is lost, ionizing the molecule and obtaining the

triaminocyclopropenium cation. Kinetic data for this reaction could not be obtained as the process is too rapid.

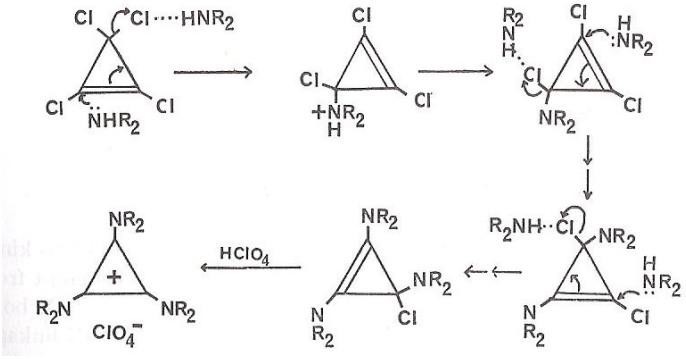


Figure 1.11 – Mechanism proposed by Yoshida[59]

Later, Clark *et al.*[73] followed the reaction between piperidine and C_3Cl_4 by ^{13}C-NMR, detecting two intermediates. The first gave signals at 59.9 and 121.0 ppm, which is similar to tetrachlorocyclopropene which has signals at 62.5 (CCl_2) and 122.0 ppm (ClC=CCl), suggesting a molecule of cyclopropene type, proposed to be $C_3(NC_5H_{10})_2C1_2$ – although they may also match $C_3N_5H_{10}Cl_3$, the first intermediate in Yoshida's proposed mechanism. While this was still present, a second intermediate gave signals at 93.3 and 131.2 ppm, which is similar to $[C_3(NPr_2)_2Cl]^+$ at 93.2 (CCl) and 131.8 ppm ($R_2NC{=}CNR_2$). The mechanism that is then proposed (Figure 1.12) is the amine attacks the vinylic carbon, displacing the chloride, attached at that carbon, and after the second amino group is added at the other vinylic position the molecule is ionized by losing Cl^- from CCl_2.

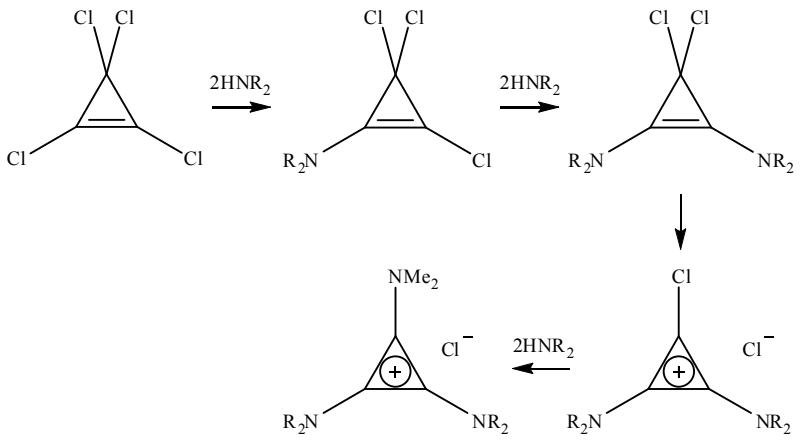
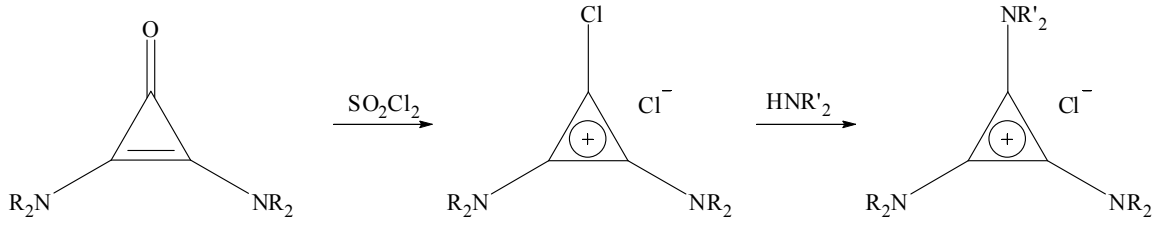


Figure 1.12 – Mechanism proposed by Clark[73]

If less symmetric cations are required, there are four synthetic routes that have been described.[59] The first route involves isolating bis(dialkylamino)chlorocyclopropenium, which can then react with another amine that is added. However, the only bis(dialkylamino)chlorocyclopropenium cations that are easily accessible are chlorobis(diisopropylamino)cyclopropenium, as was first reported by Yoshida,[63] or similar cations with bulky substituents such as chlorobis(dicyclohexylamino)cyclopropenium.

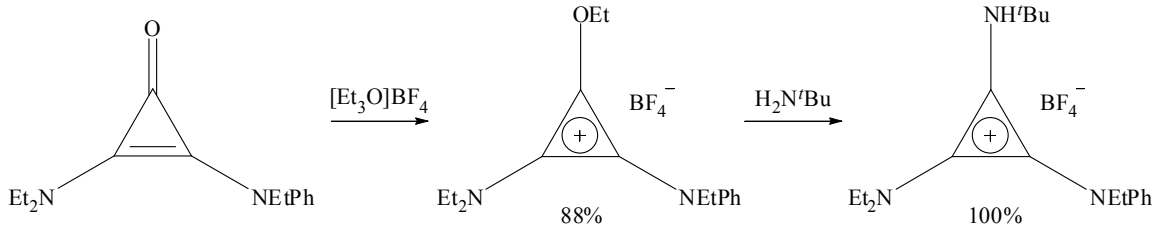
The second route is to start with bis(dialkylamino)cyclopropenones, react this with thionylchloride to form bis(dialkylamino)chorocyclopropenium, and this is then reacted with a primary or secondary amine to form a triaminocyclopropenium salt (Scheme 4).



Scheme 4 – Reaction of bis(dialkylamino)cyclopropenone with thionyl chloride, followed by reaction with dialkylamine

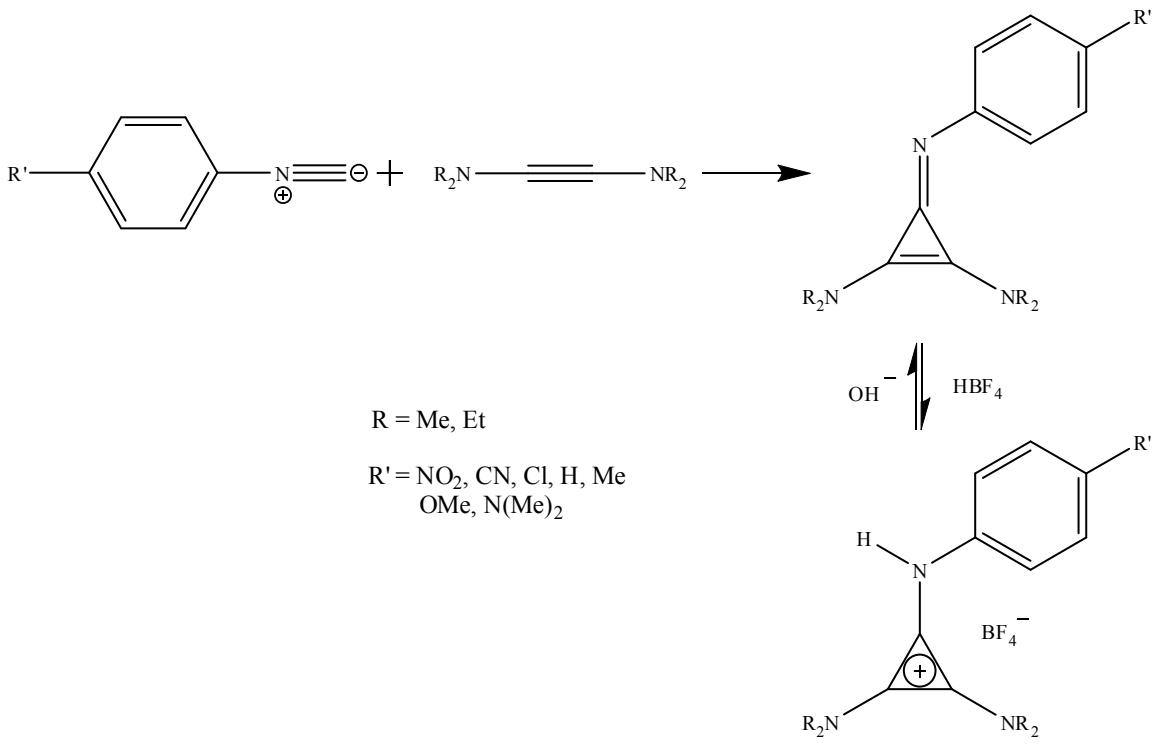
The third route is to alkylate bis(dialkylamino)cyclopropenone to form a bis(dialkylamino)alkyloxycyclopropenium. Any number of strong alkylating agents could

be used, although in the literature trialkyloxonium tetrafluoroborate is most common.[98,99] The bis(dialkylamino)alkyloxycyclopropenium will readily react with a primary or secondary amine to form a triaminocyclopropenium salt. This route was utilized by Krebs[99] to form the only example of a triaminocyclopropenium cation with three different amino substituents. Diethylaminoethylphenylaminocyclopropenone was alkylated with $[Et_3O]BF_4$ (88% yield), and tert-butylamine was added to form a triaminocyclopropenium cation (100% yield) (Scheme 5).



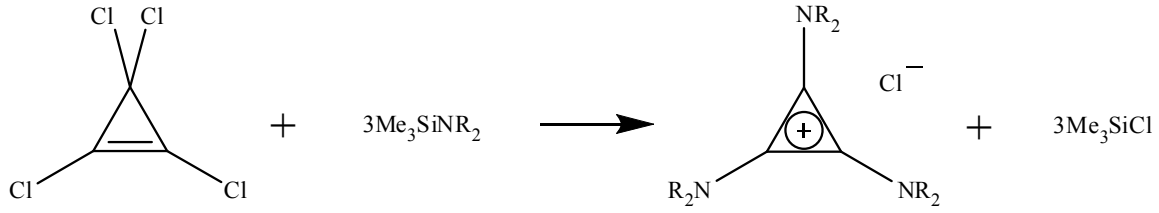
Scheme 5 – Alkylation of diethylaminoethylphenylaminocyclopropenone and substitution with ter-butylamine forming a triaminocyclopropenium cation

The fourth route to lower symmetry triaminocyclopropenium salts is via a [1+2] cycloaddition reaction (Scheme 6). This was utilized by Krebs,[99] arylisocyanides undergo a [1+2] cycloaddition reaction with bis(dialkylamino)acetylenes to form bis(dialkylamino)cyclopropenimines, with a yield of between 21 and 83%. After protonation with acid or alkylation with trialkyloxonium tetrafluoroborate, a triaminocyclopropenium cation is formed.



Scheme 6 – [1+2] cycloaddition reaction for synthesis of triaminocyclopropenium cations

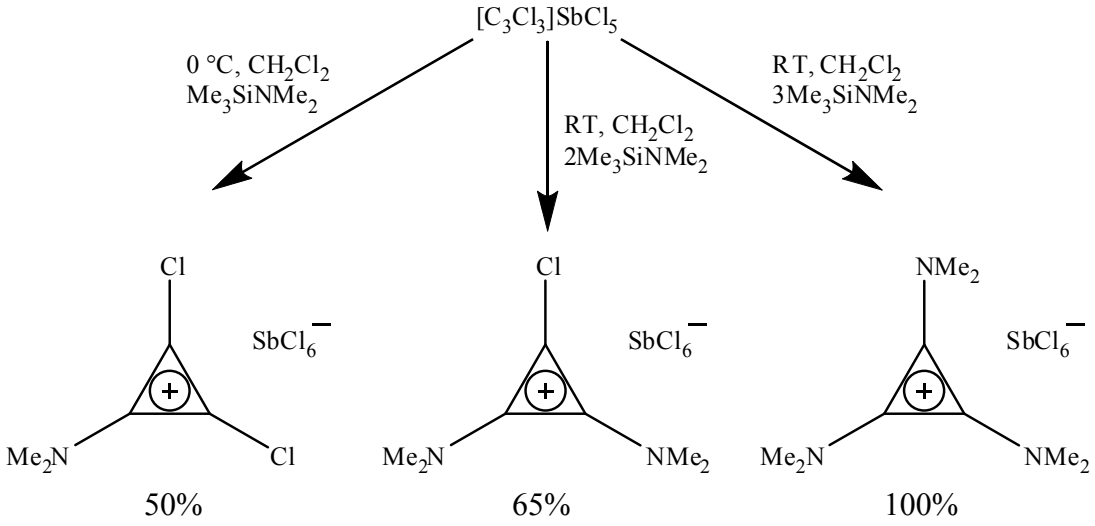
In a similar synthesis to Yoshida's, Weiss[91] used silyl amines and tetrachlorocyclopropene to make tris(dialkylamino)cyclopropeniums (Scheme 7), which reacted quantitatively and had the advantage that the byproduct is a silylchloride, which can be removed by vacuum, and so the workup does not expose the product to water.



Scheme 7 – Reaction of tetrachlorocyclopropene and trimethylsilyldialkylamines

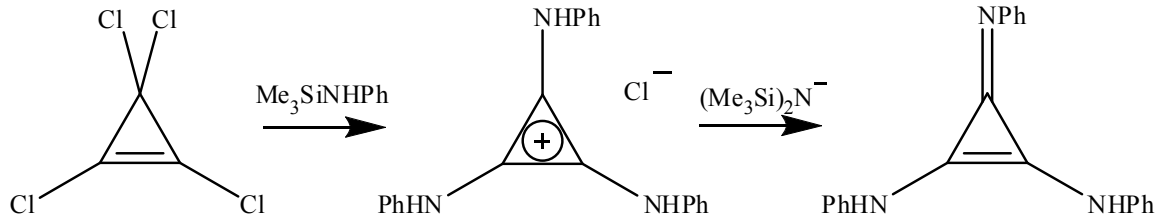
Weiss has reported anion control of the substitution[100] when reacting $[C_3Cl_3]SbCl_6$ and trimethylsilyldimethylamine (Scheme 8). By controlling the stoichiometry of the trimethylsilyldimethylamines and temperature, mono-, bis- and tris-(dimethylamino)cyclopropeniums were all synthesized. It was seen that

dichloro(dimethylamino)cyclopropenium disproportionates to chlorobis(dimethylamino)cyclopropenium in solution. As could be expected, the NMR methyl peak is more downfield for mono-, further upfield for bis- and further up again for tris(dimethylamino)cyclopropenium. The methyl peak for chlorobis(dimethylamino)cyclopropenium was split into two signals, due to the higher barrier to rotation of C-N. When the synthesis was attempted with Cl^-, BF_4^- or OTf^- anions, all gave exclusively tris(dialkylamino)cyclopropenium under the same conditions.



Scheme 8 – Anion control of amino substituent pattern

Weiss also synthesized[101] the first triaminocyclopropenium cation with protons on all three amino substituents, tris(phenylamino)cyclopropenium. Tetrachlorocyclopropene was reacted with three equivalents of trimethylsilylphenylamine (Scheme 9). The product was easily deprotonated to bis(phenylamino)cyclopropenimine with sodium bis(trimethylsilyl)amide, although at ambient temperature this will decompose over time. The ^{13}C-NMR of the imine showed only one C_3 peak, which indicated rapid proton exchange.



Scheme 9 – Synthesis and deprotonation of tris(phenylamino)cyclopropenium

However, when a primary amine[102] (^{t}BuNH$_2$ or ^{i}PrNH$_2$) is reacted with pentachlorocyclopropane, a ring opened allyl cation is formed, with four amine groups attached (Figure 1.13).

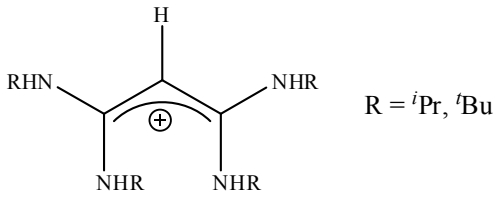


Figure 1.13 – Methylenebis(dialkylformamidinium) cation

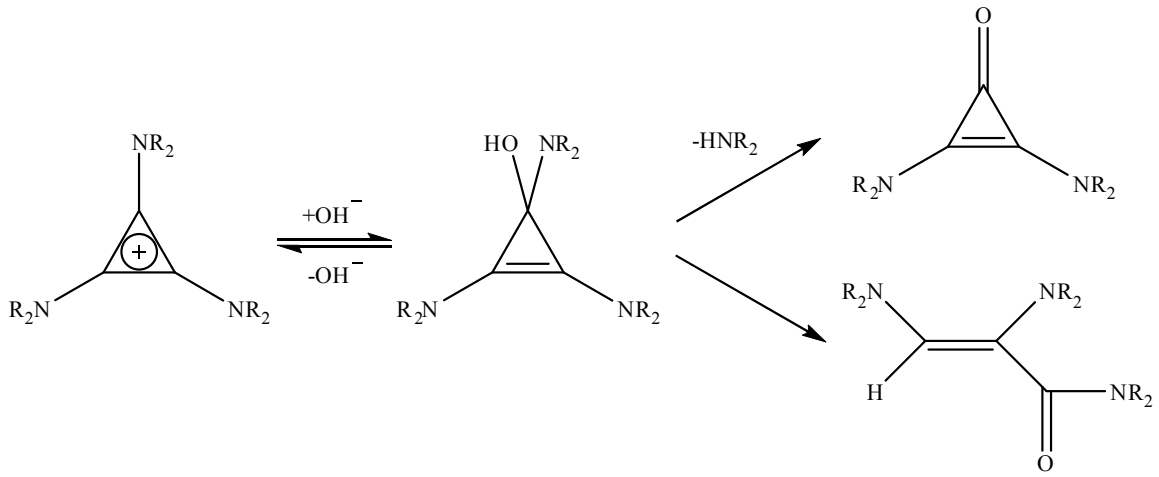
Tetrachlorocyclopropane is synthesized from pentachlorocyclopropane, however, the dehydrohalogenation using KOH has side hydrolysis reactions, lowering the yield. Taylor *et al.*[103] has studied reactions of pentachlorocyclopropane and found that the basicity of dialkylamines is enough to dehydrohalogenate it. This simplifies the overall synthesis of triaminocyclopropeniums.

The Curnow group was able to prepare the sterically-crowded tris(diisopropylamino)cyclopropenium cation[74,75] in low yield by heating diisopropylamine and pentachlorocyclopropane in dichloroethane to reflux. In solution, the isopropyl groups are all equivalent due to rotation, however, once crystallized, one amino group is forced out of the plane of the ring, thus losing back donation and becomes closer to sp^3 hybridization. [C$_3$(N^{i}Pr$_2$)$_2$NMe$_2$]ClO$_4$ was also prepared and crystallized, which showed all three amino groups are able to be planar.

1.2.4 Reactions of triaminocyclopropeniums

Triaminocyclopropenium cations are not highly reactive, although, they can undergo a variety of reactions, mostly involving nucleophilic attack on a ring carbon, generally followed by ring opening or loss of the amino group. Triaminocyclopropenium ionic liquids will therefore not be useful under certain conditions.

The most common reaction of triaminocyclopropenium is hydroxide attack to make bis(dialkylamino)cyclopropenones. Triaminocyclopropenium is stable even in refluxing water, however, even at ambient temperature in basic environments bis(dialkylamino)cyclopropenone is formed.[59,84,81] The first step (Scheme 10) of the hydrolysis is nucleophilic attack of hydroxide at the C_3 ring to generate a cyclopropene. This can either break the C-N bond, losing HNR_2 and forming the cyclopropenone, or it can break a ring C-C bond to form an acrylamide.

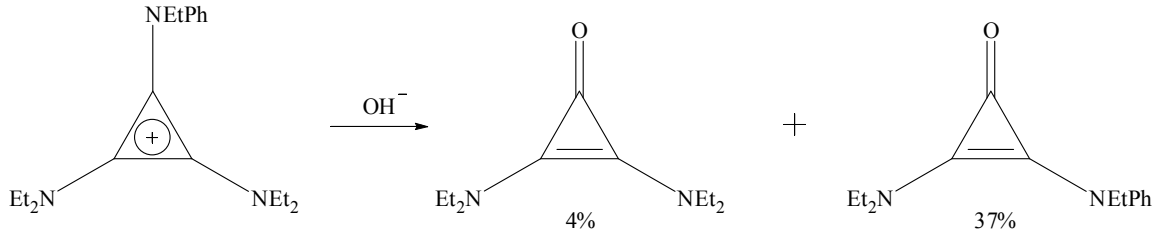


Scheme 10 – Reaction of triaminocyclopropenium and hydroxide

The product distribution depends on the basicity of the amino group, the base used and its concentration.[84] In the reaction between hydroxide and tris(methylphenylamino)cyclopropenium, the acrylamide is formed in 65% yield, while the bis(methylphenylamino)cyclopropenone is formed in 22% yield. This is due to the relatively low basicity of the methylphenylamino groups, which discourages the breaking of the C-N bond. With more basic amino groups, such as diethyl- or dimethyl-amino,

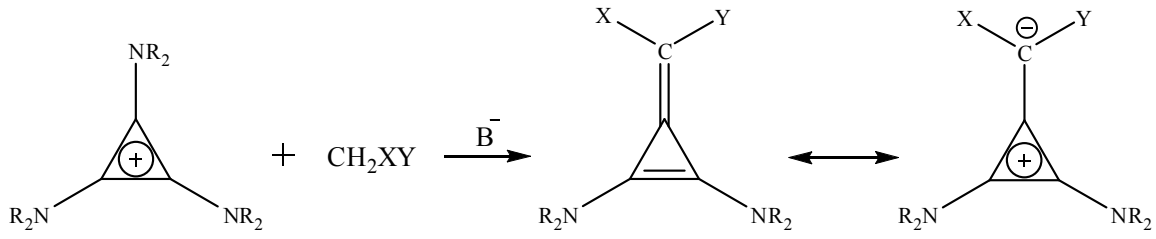
Wilcox[89] isolated bis(diethylamino)cyclopropenone and bis(dimethylamino)cyclopropenone in 81% and 91% yield, respectively.

This influence of basicity can be utilized to give mixed diamino cyclopropenones, as was done by Krebs.[99] Bis(diethylamino)ethylphenylaminocyclopropenium was reacted with hydroxide to form a mixture of cyclopropenone products (Scheme 11). While a random distribution of hydroxide attack would mean a 2:1 product ratio of diethylaminoethylphenylaminocyclopropenone and bis(diethylamino)cyclopropenone, the observed product ratio favors the mixed amino cyclopropenone 37:4



Scheme 11 – Synthesis of diethylaminoethylphenylaminocyclopropenone

A wide range of nucleophiles have been found to react with triaminocyclopropenium salts. Triaminocyclopropenium cations will react with activated methylene compounds,[88,104-106] forming a diaminotriafulvene, which has a large zwitterionic character (Scheme 12).

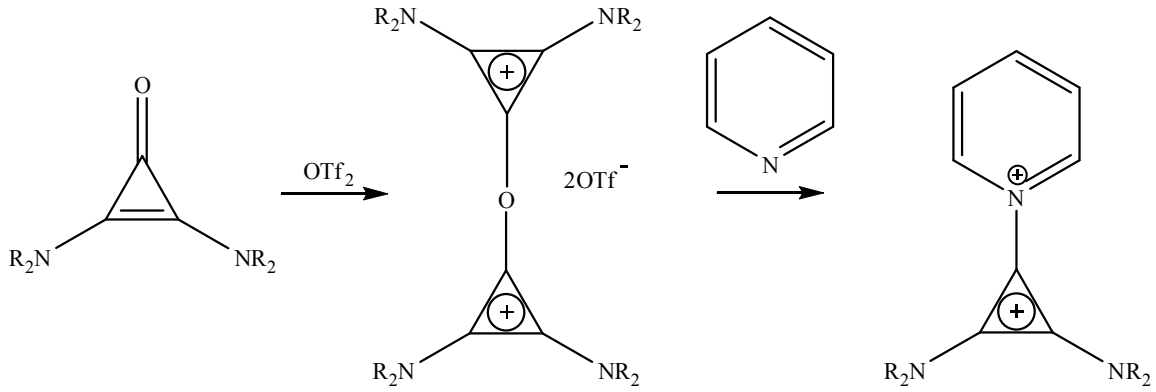


Scheme 12 – Nucleophilic reaction of triaminocyclopropenium with methylene compounds. X, Y = electron withdrawing groups

In a similar fashion, triaminocyclopropenium cations can react with nucleophiles such as iminopyridinium ylides,[107] sodium sulfide[84] and sodium selenide,[85] forming

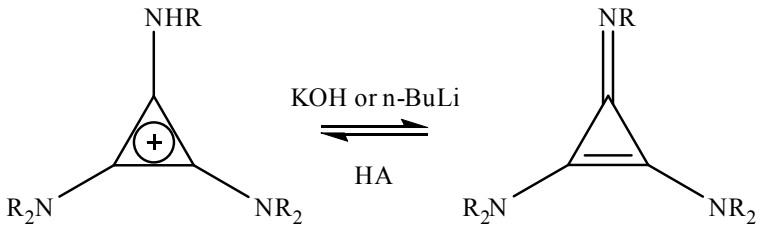
bis(dialkylamino)cyclopropenimine, bis(dialkylamino)cyclopropenethione and bis(dialkylamino)cyclopropeneselenone, respectively.

When bis(dialkylamino)cyclopropenone is treated with triflic anhydride, a dicyclopropenium dication ether is formed.[108] If treated with pyridine, a cyclopropenium pyridinium dication is formed (Scheme 13).[105]



Scheme 13 – Synthesis of diaminocyclopropenium pyridinium dications

Another point of reactivity for triaminocyclopropenium cations with secondary amino substituents is at the NH proton. This can easily be deprotonated with a strong base, such as KOH or butyl lithium, and reprotonated with acid[99] (Scheme 14). The cyclopropenium ring increases proton affinity due to the aromatization of the ring and conjugation from other amino groups when imino nitrogen is protonated.[109] In a recent paper, a chiral bis(dialkylamino)cyclopropenimine has been used as an enantioselective Brönsted base catalyst.[110] Bis(dialkylamino)cyclopropenimine can also be easily alkylated to form a hexalkyl triaminocyclopropenium.[99]



Scheme 14 – Conversion between bis(dialkylamino)cyclopropenimine and triaminocyclopropenium

1.3 References

(1) Seddon, K. R. In *The International George Papatheodorou Symposium: Proceedings*; Boghosian, S., Dracopoulos, V., Kontoyannis, C. G., Voyiatzis, G. A., Eds. **1999**.

(2) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH, **2008**.

(3) Wilkes, J. S. *Green Chem.* **2002**, *4*, 73-80.

(4) Weingartner, H. *Angew. Chem. Int. Ed.* **2008**, *47*, 654-670.

(5) Hayes, R.; Warr, G. G.; Atkin, R. *Phys. Chem. Chem. Phys.* **2010**, *12*, 1709-1723.

(6) Abbott, A. P.; Capper, G.; Davies, D. L.; Rasheed, R. K.; Tambyrajah, V. *Chem. Commun.* **2003**, 70-71.

(7) Belieres, J. P.; Angell, C. A. *J. Phys. Chem. B* **2007**, *111*, 4926-4937.

(8) Zhao, C.; Burrell, G.; Torriero, A. A. J.; Separovic, F.; Dunlop, N. F.; MacFarlane, D. R.; Bond, A. M. *J. Phys. Chem. B* **2008**, *112*, 6923-6936.

(9) Greaves, T. L.; Drummond, C. J. *Chem. Rev.* **2008**, *108*, 206-237.

(10) Wilkes, J. S. *J. Chem. Soc., Chem. Commun.* **1992**, 965-967.

(11) Seddon, K. R.; Stark, A.; Torres, M.-J. In *Clean solvents: alternative media for chemical reactions and processing*; American Chemical Society: **2002**.

(12) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. *J. Phys. Chem. B* **2005**, *109*, 6103-6110.

(13) Bandres, I.; Giner, B.; Gascon, I.; Castro, M.; Lafuente, C. *J. Phys. Chem. B* **2008**, *112*, 12461-12467.

(14) Crosthwaite, J. M.; Muldoon, M. J.; Dixon, J. K.; Anderson, J. L.; Brennecke, J. F. *J. Chem. Thermodyn.* **2005**, *37*, 559-568.

(15) Sun, J.; Forsyth, M.; MacFarlane, D. R. *J. Phys. Chem. B* **1998**, *102*, 8858-8864.

(16) Welton, T. *Chem. Rev.* **1999**, *99*, 2071-2083.

(17) Tsunashima, K.; Sugiya, M. *Electrochem. Commun.* **2007**, *9*, 2353-2358.

(18) Kunkel, H.; Maas, G. *Eur. J. Org. Chem.* **2007**, 3746-3757.

(19) Mateus, N. M. M.; Branco, L. C.; Lourenço, N. M. T.; Afonso, C. A. M. *Green Chem.* **2003**, *5*, 347-352.

(20) Branco, L. s. C.; Gois, P. M. P.; Lourenc¸o, N. M. T.; Kurtevaa, V. B.; Afonso, C. A. M. *Chem. Commun.* **2006**, 2371-2372.

(21) Carrera, G. a. V. S. M.; Branco, L. s. C.; Aires-de-Sousa, J.; Afonso, C. A. M. *Tetrahedron* **2008**.

(22) Christe, K. O.; Jenkins, H. D. B. *J. Am. Chem. Soc.* **2003**, *125*, 9457-9461.

(23) Kulkarni, P. S.; Branco, L. C.; Crespo, J. G.; Nunes, M. C.; Raymundo, A.; Afonso, C. A. M. *Chem. Eur. J.* **2007**, *13*, 8478-8488.

(24) Fang, S.; Yang, L.; JixianWang; Li, M.; Tachibana, K.; Kamijima, K. *Electrochimica Acta* **2009**, *54*, 4269-4273.

(25) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. *J. Phys. Chem. B* **2004**, *108*, 16593-16600.

(26) Matsumoto, K.; Hagiwara, R. *J. Fluorine Chem.* **2007**, *128*, 317-331.

(27) Earle, M. J.; Esperanc, J. M. S. S.; Gilea, M. A.; Lopes, J. N. C.; Rebelo, L. s. P. N.; Magee, J. W.; Seddon, K. R.; Widegren, J. A. *Nature* **2006**, *439*, 831-834.

(28) Armstrong, J. P.; Hurst, C.; Jones, R. G.; Licence, P.; Lovelock, K. R. J.; Satterley, C. J.; Villar-Garcia, I. J. *Phys. Chem. Chem. Phys.* **2007**, *9*, 982-990.

(29) Plechkovaa, N. V.; Seddon, K. R. *Chem. Soc. Rev.* **2008**, *37*.

(30) Baranyai, K. J.; Deacon, G. B.; MacFarlane, D. R.; Pringle, J. M.; Scott, J. L. *Aust. J. Chem.* **2004**, *57*, 145-147.

(31) Fredlake, C. P.; Crosthwaite, J. M.; Hert, D. G.; Aki, S. N. V. K.; Brennecke, J. F. *J. Chem. Eng. Data* **2004**, *49*, 954-964.

(32) Wooster, T. J.; Johanson, K. M.; Fraser, K. J.; MacFarlane, D. R.; Scott, J. L. *Green Chem.* **2006**, *8*, 691-696.

(33) Kamavaram, V.; Reddy, R. G. *Int. J. Therm. Sci.* **2008**, *47*, 773-777.

(34) Sesto, R. E. D.; McCleskey, T. M.; Macomber, C.; Ott, K. C.; Koppisch, A. T.; Baker, G. A.; Burrell, A. K. *Thermochimica Acta* **2009**.

(35) Schneider, S.; Hawkins, T.; Rosander, M.; Vaghjiani, G.; Chambreau, S.; Drake, G. *Energy Fuels* **2008**, *22*, 2871-2872.

(36) Gao, H.; Joo, Y.-H.; Twamley, B.; Zhou, Z.; Shreeve, J. n. M. *Angew. Chem. Int. Ed.* **2009**, *48*, 2792-2795.

(37) Abbott, A. P.; Capper, G.; Davies, D. L.; Rasheed, R. K. *Chem. Eur. J.* **2004**, *10*, 3769-3774.

(38) Bates, E. D.; Mayton, R. D.; Ntai, I.; Jr., J. H. D. *J. Am. Chem. Soc.* **2002**, *124*, 926-927.

(39) Anthony, J. L.; Anderson, J. L.; Maginn, E. J.; Brennecke, J. F. *J. Phys. Chem. B* **2005**, *109*, 6366-6374.

(40) Soutullo, M. D.; Odom, C. I.; Wicker, B. F.; Henderson, C. N.; Stenson, A. C.; James H. Davis, J. *Chem. Mater.* **2007**, *19*, 3581-3583.

(41) Anderson, J. L.; Dixon, J. K.; Brennecke, J. F. *Acc. Chem. Res.* **2007**, *40*, 1208-1216.

(42) Kumełan, J.; Kamps, A. P.-S.; Tuma, D.; Maurer, G. *Fluid Phase Equilib.* **2007**, *260*, 3-8.

(43) Tempel, D. J.; Henderson, P. B.; Brzozowski, J. R.; Pearlstein, R. M.; Cheng, H. *J. Am. Chem. Soc.* **2008**, *130*, 400-401.

(44) Olivier-Bourbigou, H.; Magna, L.; Morvan, D. *Appl. Catal., A* **2010**, *373*, 1-56.

(45) Vitz, J.; Erdmenger, T.; Haenscha, C.; Schubert, U. S. *Green Chem., 2009, 11, 417–424* **2009**, *11*, 417-424.

(46) Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. *J. Am. Chem. Soc.* **2002**, *124*, 4974-4975.

(47) Fort, D. A.; Remsing, R. C.; Swatloski, R. P.; Moyna, P.; Moyna, G.; Rogers, R. D. *Green Chem.* **2007**, *9*, 63-69.

(48) Earle, M. J.; Katdare, S. P.; Seddon, K. R. *Org. Lett* **2004**, *6*, 707-710.

(49) Endres, F.; MacFarlane, D.; Abbott, A. *Electrodeposition from ionic liquids*; Wiley-VCH, **2008**.

(50) Galiaski, M.; Lewandowski, A.; Stepniak, I. *Electrochimica Acta* **2006**, *51*, 5567-5580.

(51) Ohno, H. *Electrochemical Aspects of Ionic Liquids*; John Wiley & Sons, **2005**.

(52) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. *Green Chem.* **2001**, *3*, 156-164.

(53) Earle, M. J.; Gordon, C. M.; Plechkova, N. V.; Seddon, K. R.; Welton, T. *Anal. Chem.* **2007**, *79*, 758-764.

(54) Seddon, K. R.; Stark, A.; Torres, M. J. *Pure Appl. Chem.* **2000**, *72*, 2275-2287.

(55) Schroder, U.; Wadhawan, J. D.; Compton, R. G.; Marken, F.; Suarez, P. A. Z.; Consorti, C. S.; Souza, R. F. d.; Dupont, J. *New J. Chem.* **2000**, *24*, 1009-1015.

(56) Scammells, P. J.; Scott, J. L.; Singer, R. D. *Aust. J. Chem.* **2005**, *58*, 155-159.

(57) Breslow, R. *J. Am. Chem. Soc.* **1957**, *79*, 5318.

(58) Breslow, R.; Hover, H.; Chang, H. W. *J. Am. Chem. Soc.* **1962**, *84*, 3168-3174.

(59) Yoshida, Z. *Topics in Current Chemistry* **1973**, *40*, 47-72.

(60) Pittman, C. U.; Kress, A.; Patterson, T. B.; Walton, P.; Kispert, L. D. *J. Org. Chem.* **1974**, *39*, 373-378.

(61) Komatsu, K.; Kitagawa, T. *Chem. Rev.* **2003**, *103*, 1371-1427.

(62) Rappoport, Z. *The Chemistry of the Cyclopropyl Group*, **1987**.

(63) Yoshida, Z.; Tawara, Y. *J. Am. Chem. Soc.* **1971**, *93*, 2573-2574.

(64) Ku, A. T.; Sundaralingam, M. *J. Am. Chem. Soc.* **1972**, *94*, 1688-1692.

(65) Cowman, C. D.; Thibeault, J. C.; Ziolo, R. F.; Gray, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 3209-3214.

(66) Thibeault, J. C.; Ziolo, R. F.; Gray, H. B. *Cryst. Struct. Comm.* **1974**, *3*, 473.

(67) Radhakrishnan, T. P.; Engen, D. V.; Soos, Z. G. *Mol. Cryst. Liq. Cryst.* **1987**, *150b*.

(68) Radhakrishnan, T. P.; Engen, D. V.; Soos, Z. G. *J. Phys. Chem.* **1987**, *91*, 3273-3277.

(69) Schafer, H. N.; Burzlaff, H.; Grimmeiss, A. M. H.; Weiss, R. *Acta Cryst.* **1991**, *C47*, 1808-1811.

(70) Schafer, H. N.; Burzlaff, H.; Grimmeiss, A. M. H.; Weiss, R. *Acta Cryst.* **1992**, *C48*, 795-798.

(71) Schafer, H. N.; Burzlaff, H.; Grimmeiss, A. M. H.; Weiss, R. *Acta Cryst.* **1992**, *C48*, 912-913.

(72) Weiss, R.; Rechinger, M.; Hampel, F. *Zeitschrift fuer Kristallographie* **1995**, *210*, 71-72.

(73) Clark, G. R.; Surman, P. W. J.; Taylor, M. J. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1523-1528.

(74) Butchard, J. R.; Curnow, O. J.; Pipal, R. J.; Robinson, W. T.; Shang, R. *J. Phys. Org. Chem.* **2008**, *21*, 127-135.

(75) Butchard, J. R.; Curnow, O. J.; Garrett, D. J.; Maclagan, R. G. A. R. *Angew. Chem. Int. Ed.* **2006**, *45*, 7550-7553.

(76) Krebs, A.; Breckwoldt, J. *Tetrahedron Lett.* **1969**, *10*, 3797-3802.

(77) Breslow, R.; Groves, J. T. *J. Am. Chem. Soc.* **1970**, *92*, 984-987.

(78) Weiss, R.; Schwab, O.; Hampel, F. *Chem. Eur. J.* **1999**, *5*, 968-974.

(79) Gerson, F.; Plattner, G.; Yoshida, Z. *Molecular Physics* **1971**, *21*, 1027-1032.

(80) Matsumoto, K.; Hagiwara, R.; Yoshida, R.; Ito, Y.; Mazej, Z.; Benkic, P.; Zemva, B.; Tamada, O.; Yoshino, H.; Matsubara, S. *Dalton Trans.* **2004**, 144-149.

(81) Yoshida; Konishi, H.; Tawara, Y.; Qgoshi, H. *J. Am. Chem. Soc.* **1973**, *95*, 3043-3045.

(82) Yoshida, Z.; Konishi, H.; Ogoshi, H. *Israel J. Chem.* **1981**, *21*, 139-144.

(83) Yoshida, Z.-i.; Hirota, S.; Ogoshi, H. *Spectrochimica acta.* **1974**, *30A*, 1105-1114.

(84) Yoshida; Konishi, H.; Tawara, Y.; Nishikawa, K.; Ogoshi, H. *Tetrahedron Lett.* **1973**, *28*, 2619-2622.

(85) Yoshida, Z.-i.; Konishi, H.; Ogoshi, H. *J. Chem. Soc., Chem. Commun.* **1975**, 359-360.

(86) Yoshida, Z.; Ogoshi, H.; Hirota, S. *Tetrahedron Lett.* **1973**, *11*, 869-878.

(87) Yoshida, Z.; Tawara, Y.; Hirota, S.; Ogoshi, H. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 797-800.

(88) Yoshida, Z.; Tawara, Y. *Tetrahedron Letters* **1971**, *39*, 3603-3606.

(89) Wilcox, C.; Breslow, R. *Tetrahedron* **1980**, *21*, 3241-3242.

(90) Kerber, R. C.; Hsu, C.-M. *J. Am. Chem. Soc.* **1973**, *95*, 3239-3245.

(91) Weiss, R.; Sohloter, K. *Tetrahedron Lett.* **1975**, *40*, 3491-3494.

(92) Johnson, R. W. *Tetrahedron Lett.* **1976**, *8*, 589-592.

(93) Surman, P. W. J.; Anderson, R. F.; Packer, J. E.; Taylor, M. J. *J. Phys. Chem. A* **1997**, *101*, 2732-2734.

(94) Clark, T.; Weiss, R. *J. Org. Chem.* **1980**, *45*, 1790-1794.

(95) Weiss, R.; Brenner, T.; Hampel, F.; Wolski, A. *Angew. Chem. Int. Ed.* **1995**, *34*, 439-441.

(96) Weiss, R.; Hampel, M. R. F.; Wolski, A. *Anew. Chem. Int. Ed* **1995**, *34*, 441-443.

(97) Gompper, R.; Schonafinger, K. *Chem. Ber.* **1979**, *112*, 1514-1528.

(98) Schulenberg, J. W.; Patent, U., Ed. US, **1974**.

(99) Krebs, A.; Gtintner, A.; Versteylen, S.; Schulz, S. *Tetrahedron Lett.* **1984**, *25*, 2333-2336.

(100) Weiss, R. *Tetrahedron Lett.* **1979**, *35*, 3295-3296.

(101) Weiss, R.; Hertel, M. *J. Chem. Soc., Chem. Commun.* **1980**, 223-224.

(102) Clark, G. R.; Rickard, C. E. F.; Surman, P. W. J.; Taylor, M. J. *J. Chem. Soc., Faraday T rans.* **1997**, *93*, 2503-2507.

(103) Taylor, M. J.; Surman, P. W. J.; Clark, G. R. *J. Chem. Soc., Chem. Commun.* **1994**, 2517-2518.

(104) Weber, H.-M.; Maas, G. *Chem. Ber.* **1988**, *121*, 1791-1794.

(105) Weber, H.-M.; Maas, G. *Synthesis* **1988**, *8*, 604-608.

(106) Weiss, R.; Lowack, R. H. *Bull. Soc. Chim. Belg.,* **1991**, *100*, 483-486.

(107) Inoue, S.; Gorou Yasuda, a. T. H. *Chem. Lett.* **1976**, 1215-1216.

(108) Maas, G.; Stang, P. J. *J. Org. Chem.* **1983**, *48*, 3038-3043.

(109) Maksic, Z. B.; Kovacevic, B. *J. Phys. Chem. A* **1999**, *103*, 6678-6684.

(110) Bandar, J. S.; Lambert, T. H. *J. Am. Chem. Soc.* **2012**, *134*, 5552-5555.

Chapter 2

2 Experimental

2.1 General procedures

2.1.1 Synthesis

Synthesis of triaminocyclopropenium salts from pentachlorocyclopropane or bis(dialkylamino)cyclopropenone was carried out under an inert dinitrogen atmosphere using standard Schlenk line techniques. Where dry solvents were needed, dried analytical reagent grade solvent was used. Lithium bis(trifluoromethanesulfonyl)amide (3M) was provided by Professor Ken Marsh. All other reagents were obtained from commercial sources.

2.1.2 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) was carried out on a TA Q100 DSC and a Perkin-Elmer DSC 8000. The DSC 8000 was calibrated with indium (156.60 °C) and cyclohexane (-87.0 and 6.5 °C). Three heating and cooling cycles were carried out with data collected off a repeatable second cycle. A scan rate of 10 °C min^{-1} was used, over a temperature range of at least –100 to 50 °C, with a greater range used as required. Transition temperatures are reported as the onset temperature. Enthalpy for a transition was found by integrating the peak area, with entropy then calculated using $\Delta S = \Delta H/T$. Sample size was approximately 5 to 10 mg.

2.1.3 Density

Density measurements were carried out on an Anton Parr DMA 5000 instrument, an oscillating U-tube density meter, from 20 to 90 °C in 10 °C steps.

2.1.4 Viscosity

Viscosity of $[C_3(NPr_2)_3]DCA$, $[C_3(NBu_2)_3]Cl$, $[C_3(NBu_2)_3]DCA$, $[C_3(NBu_2)_3]OTf$, $[C_3(NBu_2)_3]TFSA$, $[C_3(NHex_2)_3]DCA$, $[C_3(NHex_2)_3]TFSA$, $[C_3(NEt_2)_2NMe_2]TFSA$ and all imidazolium fluoride acetic acid mixtures were measured on an Anton Parr AMVn

automated microviscometer, a falling ball viscometer. All other samples were measured on a Brookfield DV-II+ Pro cone and plate viscometer. Samples that were measured using the cone and plate viscometer were examined for non-Newtonian behaviour, although this was only over a limited shear rate range. All samples were measured from 20 (or above the melting point if solid) to 80 or 90 °C, and performed sealed or under a dinitrogen gas flow.

2.1.5 Conductivity

Conductivity of $[C_3(NEt_2)_3]ClO_4$, $[C_3(NBu_2)_3]NO_3$, $[C_3(NPent_2)_3]DCA$, $[C_3(NPent_2)_3]TFSA$, $[C_3(NDec_2)_3]DCA$, $[C_3(NDec_2)_3]TFSA$, $[C_3(NEt_2)_2NHexMe]DCA$ and $[C_3(NEt_2)_2NHexMe]TFSA$ was measured using a Schott LF4100+ probe, an impedance bridge conductivity meter. The instrument was calibrated with 0.1 mol L^{-1} KCl solution. All other conductivities were measured by AC impedance spectroscopy on a Solatron SI 1296 frequency response analyser, at ranges up to 0.01 Hz to 10 MHz. Measurements were carried out with a dip cell probe containing two platinum wires covered in glass. The resistance was identified using a Nyquist Plot, and conductivity then calculated using $\kappa = \frac{l}{AR}$, where $\frac{l}{A}$ is the cell constant, which was determined using 0.01 mol L^{-1} KCl solution at 25 °C. All samples were measured from 20 (or above the melting point if solid) to 80 or 90 °C, and performed sealed or under a dinitrogen gas flow.

The standard deviation of the fitted equations compared to measured viscosity, conductivity and density data was calculated using the sample standard deviation:

Equation 1 – Sample standard deviation

$$\delta = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}\left(x_i - x_{calc}\right)^2}$$

2.1.6 Thermal Gravimetric Analysis

Thermal Gravimetric Analysis (TGA) was carried out on a TA Q600 SDT (simultaneous DSC-TGA), using platinum pans. Temperature calibration carried out using zinc (419.6 °C), and heat flow using a sapphire standard. Pans were cleaned after each TGA experiment by heating at 500 °C under an air atmosphere, and if required cleaned with nitric acid. Sample size was approximately 10 mg.

2.1.7 Chemical Stability

Chemical stability tests were conducted by placing 250 mg samples of $[C_3(NEt_2)_3]Cl$, $[C_3(NEt_2)_3]DCA$ and $[C_3(NEt_2)_3]TFSA$ together with an equimolar amount of HCl (38%, aq), NH_3 (40%, aq, 2 equivalents), KOH, $NaBH_4$, $NaIO_4$ or EtMgI, and stirred at ambient temperature or heated to 60 °C. After 24 hours, ^{1}H-NMR was used to assess whether any degradation of the triaminocyclopropenium cation had occurred. The samples were also heated at 100 and 150 °C for 24 hours while exposed to an open atmosphere.

2.1.8 Cyclic Voltammetry

Cyclic voltammetry was carried out using an Eco Chemie Autolab PGSTAT 302N potentiostat running GPES 4.9 software. A platinum working electrode (1.2 mm diameter), platinum wire secondary electrode and silver wire reference electrode were used. Recrystallized $[C_3(NEt_2)_3]TFSA$ was dried under vacuum at 50 °C for 72 hours, which reduced water content to 71 ppm, measured by a coulombic Karl-Fischer titrator. Sample was degassed by bubbling with argon for 60 min before the experiment, and kept under an argon atmosphere for the experiments. Once the electrochemical window was measured, ferrocene was added to the ionic liquid as an internal reference.

2.1.9 Solubility

Solubility tests were carried out using a 25 °C water bath. For liquid samples, 0.5 mL of the ionic liquid was taken, and 0.05 mL of dry analytical reagent grade solvent was added ten times, followed by 0.5 mL nine times. After each addition of solvent, the layers were mixed, and with immiscible or insoluble mixtures a solvent layer would reform. For solid

samples, 0.1 g samples were taken, and 2.5 mL of solvent added. If the solid remained then the sample was insoluble, if the solid liquidified then it was immiscible or if the solid dissolved then it was soluble.

2.1.10 NMR

^{1}H-, ^{13}C{^{1}H}-NMR spectra were collected on a Varian Unity-300 operating at 300 and 75 MHz respectively, or on a Varian INOVA-500 operating at 500 and 126 MHz respectively, in $CDCl_3$ or D_2O, referenced to residual solvent peaks or TMS. ^{19}F-NMR spectra were collected on a Varian Unity-300 operating at 282 MHz, in $CDCl_3$ or D_2O, referenced to C_6H_5F or $CFCl_3$.

2.1.11 Mass Spectrometry

A maXis 3G UHR-Qq-TOF mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) was used; this was coupled to a Dionex Ultimate 3000 LC system (ThermoFisher). 5 uL of sample was injected into a flow of 50:50 water(0.5% formic acid):acetonitrile at 0.2mL/min to the mass spectrometer. For each acquisition, 5uL of a calibrant of ESI-L Low Concentration Tuning Mix (Agilent Technologies) was injected after each sample. The observed mass and isotope pattern matched the corresponding theoretical values as calculated from the expected elemental formula.

2.1.12 Microanalysis

Microanalysis was performed by Campbell Microanalytical Laboratory, Dunedin.

2.1.13 Karl-Fischer Titrator

Water content was measured with a Metrohm 831 Karl-Fischer Coulometer.

2.2 Syntheses of triaminocyclopropenium salts

2.2.1 Pentachlorocyclopropane[1]

Sodium trichloroacetate (501 g, 2.70 mol) was added to trichloroethene (1.65 L, 18.3 mol) and brought to reflux, with a Dean-Stark apparatus attached. Water forms a

heteroazeotrope with trichloroethene, and reflux was continued for 3 h until water had been removed. Dimethoxyethane (260 mL, 2.51 mol) was dried (distilled from CaH_2), and added to the trichloroethene solution. The reaction was heated to reflux and stirred for 7 days. The solution was washed with water (3 x 1 L), then with dilute HCl (0.1 mol L^{-1}, 3 x 1 L) and again with water (3 x 1 L). Excess trichloroethene was removed with a rotary evaporator, and pentachlorocyclopropane (125 mL, 36% yield) was isolated from the crude product via distillation under reduced pressure.

2.2.2 Bis(diethylamino)cyclopropenone[2]

KOH (300 g) was dissolved into water (4 L). Tris(diethylamino)cyclopropenium chloride (42 g, 0.15 mol) was added to the solution, and heated to 70 °C for 18 h. Organic compounds were extracted from aqueous solution using dichloromethane (3 x 250 mL). Dichloromethane was removed *in vacuo* and the pH of the residue was neutralized using a small amount of HCl. Ethanol (25 mL) added to allow filtering to remove insoluble impurities, followed by removing ethanol *in vacuo*. Addition of acetone (75 mL) precipitated KCl, which was filtered off. Acetone was removed *in vacuo*, yielding a dark orange liquid (22 g, 77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.21 (q, $^3J_{HH}$ = 7.2 Hz, 8H, NCH_2CH_3), 1.20 (t, $^3J_{HH}$ = 7.2 Hz, 12H, NCH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 133.74 (CO), 119.32 (C_2), 46.01 (NCH_2CH_3), 14.18 (NCH_2CH_3).

2.2.3 Tris(dimethylamino)cyclopropenium chloride, $[C_3(NMe_2)_3]Cl$[3,4]

C_3Cl_5H (3.53 g, 16.5 mmol) was dissolved in dichloromethane (100 mL) and cooled to 0 °C. $HNMe_2$ (10.2 g, 226 mmol) was added dropwise and the solution was allowed to warm to ambient temperature and stirred overnight. The solution was heated to reflux for 3 h, before dichloromethane and excess amine was removed *in vacuo*. An acetonitrile/toluene mixture (1:2 volume ratio, 125 mL) was added and cooled in the freezer. The $[H_2NMe_2]Cl$ precipitate was filtered off and the precipitation process repeated. Removal of the acetonitrile/toluene *in vacuo* yielded an orange solid (1.81 g, 54% yield). ^{1}H NMR (500 MHz, $CDCl_3$): 3.16 (s, NCH_3). ^{13}C NMR (126 MHz, $CDCl_3$):

116.76 (C_3), 42.11 (N*C*H$_3$). ES$^+$ m/z 168.4199 (100%, M$^+$). Found: C, 46.92; H, 9.47; N, 16.49%. Calc. for $C_9H_{18}N_3Cl.1.50H_2O$: C, 46.84; H, 9.17; N, 18.21%.

2.2.4 Tris(dimethylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, [$C_3(NMe_2)_3$]TFSA

[$C_3(NMe_2)_3$]Cl (3.5 g, 17.2 mmol) was stirred with LiTFSA (15.0 g, 52.3 mmol) in water (200 mL). The product was extracted with dichloromethane/diethyl ether mixture (200 mL, 1:3), washed with water (3 x 100 mL) and dried *in vacuo* to yield colourless crystals (1.5 g, 20%). ^{1}H, ^{13}C NMR and MS$^+$ as for cation of [$C_3(NMe_2)_3$]Cl. Found: C, 29.46; H, 4.05; N, 12.49%. Calc. for $C_{11}H_{18}N_4S_2O_4F_6$: C, 29.58; H, 4.10; N, 12.28%. Cl$^-$ content: 298 ppm.

2.2.5 Tris(diethylamino)cyclopropenium chloride, [$C_3(NEt_2)_3$]Cl[3]

$HNEt_2$ (213 g, 2910 mmol) was dissolved in dichloromethane (500 mL) and cooled to 0 °C. C_3Cl_5H (66.7g, 311 mmol) was added dropwise and the solution stirred overnight at ambient temperature. The solution was heated to reflux for 4 h, before dichloromethane and excess amine was removed *in vacuo*. Acetone (200 mL) was added and the [H_2NEt_2]Cl precipitate was filtered off. After removal of acetone under vacuum, dichloromethane (200 mL) was added, and washed with dilute NaOH, then neutralized with HCl. After removal of dichloromethane under vacuum, the residual [H_2NEt_2]Cl was removed by dissolving in dichloromethane (250 mL) and washing with water (3 x 150 mL). Removal of dichloromethane *in vacuo* yielded an orange liquid which solidified overnight (77.0 g, 86% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): 3.36 (q, $^3J_{HH}$ = 7.3 Hz, 12H, NC*H$_2$*), 1.22 (t, $^3J_{HH}$ = 7.4 Hz, 18H, NCH_2CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): 115.99 (C_3), 47.07 (N*C*H$_2$CH$_3$), 14.24 (NCH_2CH_3). ES$^+$ m/z 252.2433 (100%, M$^+$). Found: C, 56.96; H, 10.12; N, 12.66; Cl, 11.93%. Calc. for $C_{15}H_{30}N_3Cl.1.58H_2O$: C, 56.96; H, 10.57; N, 12.29; Cl, 11.21%.

2.2.6 Tris(diethylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_3]TFSA$

$[C_3(NEt_2)_3]Cl$ (7.30 g, 25.4 mmol) was stirred with LiTFSA (21.8 g, 76.0 mmol) in water (200 mL). The product was extracted with chloroform (200 mL), washed with water (3 x 200 mL) and dried *in vacuo* to yield an orange liquid (11.5 g, 85%). ^1H, ^{13}C NMR and MS^+ as for $[C_3(NEt_2)_3]Cl$. Found: C, 38.80; H, 5.81; N, 10.60%. Calc. for $C_{17}H_{30}N_4S_2O_4F_6$: C, 38.34; H, 5.68; N, 10.52%. H_2O content: 196 ppm. Cl^- content: 166 ppm.

2.2.7 Tris(diethylamino)cyclopropenium dicyanamide, $[C_3(NEt_2)_3]DCA$

$[C_3(NEt_2)_3]Cl$ (8.30 g, 28.3 mmol) was stirred with NaDCA (9.50 g, 107 mmol) in water (100 mL). The product was extracted with chloroform (150 mL), washed with water (3 x 100 mL) and dried *in vacuo* to yield an orange liquid (7.88 g, 86%). ^1H, ^{13}C NMR and MS^+ as for $[C_3(NEt_2)_3]Cl$. Found: C, 63.99; H, 9.77; N, 26.59%. Calc. for $C_{17}H_{30}N_6Cl$: C, 64.12; H, 9.49; N, 26.39%. H_2O content: 1043 ppm. Cl^- content: 960 ppm.

2.2.8 Tris(dipropylamino)cyclopropenium chloride, $[C_3(NPr_2)_3]Cl$

HN^nPr_2 (88.6 g, 0.875 mol) was dissolved in dichloromethane (250 mL) and cooled to 0 °C. C_3Cl_5H (25.0 g, 0.117 mol) was added dropwise and the solution stirred overnight at ambient temperature. The solution was heated to reflux for 3 h, before dichloromethane and excess amine was removed *in vacuo*. Acetone (200 mL) was added and the $[H_2NPr_2]Cl$ precipitate was filtered off. After removal of acetone under vacuum, the residual $[H_2NPr_2]Cl$ was removed by dissolving in dichloromethane (250 mL) and washing with water (3 x 150 mL). Removal of dichloromethane *in vacuo* yielded an orange liquid which solidified overnight (36.9 g, 85%). ^1H NMR (500 MHz, $CDCl_3$): 3.25 (t, $^3J_{HH}$ = 8.0 Hz, 12H, NCH_2), 1.65 (m, 12H, NCH_2CH_2), 0.92 (t, $^3J_{HH}$ = 7.3 Hz, 18H, $NCH_2CH_2CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$): 115.98 (C_3), 52.22 (NCH_2), 21.81 (NCH_2CH_2), 10.52 (CH_3). ES^+ m/z 336.3379 (100%, M^+). Found: C, 62.01; H, 10.77; N, 9.56; Cl, 8.93%. Calc. for $C_{21}H_{42}N_3Cl.1.93H_2O$: C, 62.01; H, 11.36; N, 10.33; Cl, 8.71%.

2.2.9 Tris(dipropylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NPr_2)_3]TFSA$

$[C_3(NPr_2)_3]Cl$ (17.5 g, 47.1 mmol) was stirred with LiTFSA (40.4 g, 141 mmol) in water (100 mL). The product was extracted with chloroform (100 mL), washed with water (3 x 200 mL) and dried *in vacuo* to yield an orange liquid (24 g, 83%). ^1H, ^{13}C NMR and MS^+ as for $[C_3(NPr_2)_3]Cl$. X-ray crystal structure obtained. Found: C, 44.95; H, 6.99; N, 9.11%. Calc. for $C_{23}H_{42}N_4S_2O_4F_6$: C, 44.79; H, 6.86; N, 9.08%. H_2O content: 135 ppm. Cl^- content: 100 ppm.

2.2.10 Tris(dipropylamino)cyclopropenium dicyanamide, $[C_3(NPr_2)_3]DCA$

$[C_3(NPr_2)_3]Cl$ (7.69 g, 20.7 mmol) was stirred with aqueous NaDCA (3.73 g, 41.9 mmol) in water (100 mL). The product was extracted with dichloromethane (50 mL) and washed with water (3 x 100 mL). Additional aqueous NaDCA (1.85 g, 20.8 mmol) was added and the organic layer was then washed with water (4 x 100 mL) and dried *in vacuo* to yield a yellow liquid (11.5 g, 85%) which slowly crystallized.^1H, ^{13}C NMR and MS^+ as for $[C_3(NPr_2)_3]Cl$. X-ray crystal structure obtained. Found: C, 67.19; H, 10.57; N, 19.77%. Calc. for $C_{23}H_{42}N_6.0.6H_2O$: C, 66.82; H, 10.53; N, 20.33%. Cl^- content: 314 ppm.

2.2.11 Tris(dibutylamino)cyclopropenium chloride, $[C_3(NBu_2)_3]Cl$

$HNBu_2$ (123 g, 0.950 mol) was dissolved in dichloromethane (250 mL) and cooled to 0 °C. C_3Cl_5H (25.0 g, 0.117 mol) was added dropwise and the solution stirred overnight at ambient temperature. The solution was heated to reflux for 3 h, before dichloromethane and excess amine was removed *in vacuo*. Acetone (200 mL) was added and the $[H_2NBu_2]Cl$ precipitate was filtered off. After removal of acetone under vacuum, the residual $[H_2NBu_2]Cl$ was removed by dissolving in dichloromethane (250 mL) and washing with water (3 x 150 mL). Dichloromethane was removed *in vacuo*, and this was followed by washing the crude product with petroleum ether (4 x 50 mL) to remove residual amine. This yielded a light brown liquid (50.8 g, 96% yield) that solidified overnight. ^1H NMR (300 MHz, $CDCl_3$): 3.27 (t, $^3J_{HH}$ = 7.91 Hz, 12H, NCH_2), 1.57 (m,

12H, NCH_2CH_2), 1.29 (m, 12H, $NCH_2CH_2CH_2$), 0.91 (t, $^3J_{HH}$ = 7.03 Hz, 18H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): 116.2 (C_3), 52.6 (NCH_2), 30.7 (NCH_2CH_2), 19.6 ($NCH_2CH_2CH_2$), 13.5 (CH_3). ES^+ m/z 420.4321 (100%, M^+). Found: C, 69.09; H, 11.38; N, 9.06; Cl, 7.99%. Calc. for $C_{27}H_{54}N_3Cl.0.6H_2O$: C, 69.44; H, 11.91; N, 9.00; Cl, 7.59%.

2.2.12 Tris(dibutylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NBu_2)_3]TFSA$

$[C_3(NBu_2)_3]Cl$ (10.74 g, 23.6 mmol) was stirred with aqueous LiTFSA (7.8 g, 27.2 mmol) in water (100 mL). The product was extracted with dichloromethane (40 mL) and washed with water (2 x 40 mL). Additional aqueous LiTFSA (7.7 g, 26.8 mmol) was added, and the solution was then washed with water (3 x 30 mL) and dried *in vacuo* to yield an orange liquid (12.9 g, 78%). ^1H, ^{13}C NMR and MS^+ as for $[C_3(NBu_2)_3]Cl$. Found: C, 49.43; H, 7.92; N, 8.07%. Calc. for $C_{29}H_{54}N_4S_2O_4F_6$: C, 49.70; H, 7.77; N, 7.99%. H_2O content: 64 ppm. Cl^- content: 329 ppm.

2.2.13 Tris(dibutylamino)cyclopropenium dicyanamide, $[C_3(NBu_2)_3]DCA$

$[C_3(NBu_2)_3]Cl$ (6.00 g, 13.2 mmol) was stirred with AgDCA (7.8 g, 27.2 mmol) in water (100 mL). Dichloromethane (150 mL) was added to dissolve $[C_3(NBu_2)_3]DCA$, allowing a fine filter to be used to remove solid AgCl and the dichloromethane solution was washed with water (2 x 100 mL). The organic layer was concentrated and filtered again. It was then dried *in vacuo* to yield a yellow liquid (5.06 g, 79%). ^1H, ^{13}C NMR and MS^+ as for $[C_3(NBu_2)_3]Cl$ with an additional peak due to DCA. Found: C, 70.31; H, 11.20; N, 17.28%. Calc. for $C_{29}H_{54}N_6.0.48H_2O$: C, 70.31; H, 11.18; N, 16.96%. H_2O content: 181 ppm. Cl^- content: 100 ppm.

2.2.14 Tris(dibutylamino)cyclopropenium tetrafluoroborate, $[C_3(NBu_2)_3]BF_4$

$[C_3(NBu_2)_3]Cl$ (6.17 g, 13.6 mmol) was stirred with HBF_4 (20 mL, 35%, 110 mmol) in water (50 mL). The product was extracted with dichloromethane (75 mL) and washed again with HBF_4 (20 mL, 35%, 110 mmol). The organic layer was then washed with

water (3 x 50 mL) until the pH was neutral and dried *in vacuo* to yield an orange liquid (4.13 g, 80%). ^{1}H, ^{13}C NMR and MS^{+} as for $[C_3(NBu_2)_3]Cl$. Found: C, 63.88; H, 10.50; N, 8.14%. Calc. for $C_{27}H_{54}N_3BF_4$: C, 63.84; H, 10.72; N, 8.28%. H_2O content: 110 ppm. Cl^- content: 248 ppm.

2.2.15 Tris(dibutylamino)cyclopropenium nitrate, $[C_3(NBu_2)_3]NO_3$

$[C_3(NBu_2)_3]Cl$ (5.24 g, 11.5 mmol) was stirred with HNO_3 (10 mL, 69%, 153 mmol) in water (20 mL). The product was extracted with dichloromethane (75 mL) and washed again with HNO_3 (10 mL, 69%, 153 mmol). The organic layer was then washed with water (3 x 75 mL) until the pH was neutral and dried *in vacuo* to yield an orange liquid (4.16 g, 75%). ^{1}H, ^{13}C NMR and MS^{+} as for $[C_3(NBu_2)_3]Cl$. Found: C, 65.49; H, 11.42; N, 11.80%. Calc. for $C_{27}H_{54}N_4O_3.0.60H_2O$: C, 65.71; H, 11.27; N, 11.35%. H_2O content: 224 ppm. Cl^- content: 639 ppm.

2.2.16 Tris(dibutylamino)cyclopropenium triflate, $[C_3(NBu_2)_3]OTf$

$[C_3(NBu_2)_3]Cl$ (6.00 g, 13.2 mmol) was stirred with LiOTf (2.25 g, 14.5 mmol) in water (100 mL). The product was extracted with dichloromethane (75 mL), washed with water (5 x 100 mL), and dried *in vacuo* to yield a yellow solid (5.95 g, 79%). ^{1}H, ^{13}C NMR and MS^{+} as for cation of $[C_3(NBu_2)_3]Cl$. Found: C, 59.33; H, 9.83; N, 7.41%. Calc. for $C_{28}H_{54}N_3SO_3F_3$: C, 59.02; H, 9.55; N, 7.37%. H_2O content: 278 ppm. Cl^- content: 916 ppm.

2.2.17 Tris(dibutylamino)cyclopropenium bromide, $[C_3(NBu_2)_3]Br$

$[C_3(NBu_2)_3]Cl$ (0.86 g, 1.9 mmol) was stirred with HBr (20 mL, 38%, 140 mmol). The product was extracted with chloroform (20 mL) and washed again with HBr (20 mL, 38%, 140 mmol). It was then washed with water (3 x 20 mL) until the pH was neutral and dried *in vacuo* to yield a dark brown solid (0.50 g, 52%). ^{1}H, ^{13}C NMR and MS^{+} as for $[C_3(NBu_2)_3]Cl$. Found: C, 61.82; H, 10.37; N, 7.63%. Calc. for $C_{27}H_{54}N_3Br.1.33H_2O$: C, 61.82; H, 10.65; N, 7.72%.

2.2.18 Tris(dipentylamino)cyclopropenium chloride, $[C_3(NPent_2)_3]Cl$

Dipentylamine (11.9 g, 75.9 mmol) and NEt_3 (25 mL, 179 mmol) was added to dichloromethane (100 mL) and cooled to 0 °C. C_3Cl_5H (4.84 g, 22.6 mmol) was added dropwise and the solution stirred overnight at ambient temperature. The solution was heated to reflux for 4 h, then water added (200 mL). Solution was acidified with aqueous HCl. The dichloromethane was separated and washed with water (3 x 150 mL). Removal of dichloromethane *in vacuo* yielded a viscous orange liquid (10.6 g, 90% yield). ^1H NMR (500 MHz, $CDCl_3$): δ 3.25 (t, $^3J_{HH}$ = 7.70 Hz, 12H, NCH_2), 1.57 (m, 12H, NCH_2CH_2), 1.30 (m, 12H, $N(CH_2)_2CH_2$), 1.21 (m, 12H, $N(CH_2)_3CH_2$), 0.85 (t, $^3J_{HH}$ = 7.15 Hz, 18H, $N(CH_2)_4CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$): 116.30 (C_3), 52.86 (NCH_2), 28.50 (NCH_2CH_2), 28.45 ($N(CH_2)_2CH_2$), 22.16 ($N(CH_2)_3CH_2$), 13.67 ($N(CH_2)_4CH_3$). ES^+ m/z 504.5265 (100%, M^+). Found: C, 70.76; H, 12.22; N, 7.65%. Calc. for $C_{33}H_{66}N_3Cl.1.10H_2O$: C, 70.76; H, 12.27; N, 7.50%.

2.2.19 Tris(dipentylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NPent_2)_3]TFSA$

$[C_3(NPent_2)_3]Cl$ (3.09 g, 5.73 mmol) was stirred with aqueous LiTFSA (4.9 g, 19.9 mmol) in water (100 mL). The product was extracted with diethyl ether (200 mL), and additional LiTFSA (6.1 g, 21.3 mmol) and water (100 mL) was added. The diethyl ether solution was then washed with water (3 x 100 mL) and dried *in vacuo* to yield an orange liquid (4.30 g, 96%). ^1H, ^{13}C NMR and MS^+ as for $[C_3(NPent_2)_3]Cl$. Found: C, 54.43; H, 8.57; N, 7.23%. Calc. for $C_{35}H_{66}N_4S_2O_4F_6$: C, 53.55; H, 8.47; N, 7.14%. H_2O content: 58 ppm. Cl^- content: 198 ppm.

2.2.20 Tris(dipentylamino)cyclopropenium dicyanamide, $[C_3(NPent_2)_3]DCA$

$[C_3(NPent_2)_3]Cl$ (4.13 g, 7.66 mmol) was stirred with aqueous NaDCA (3.8 g, 43.1 mmol) in water (100 mL). The product was extracted with diethyl ether (200 mL), and additional NaDCA (6.1 g, 44.9 mmol) and water (100 mL) was added. The diethyl ether solution was then washed with water (3 x 100 mL) and dried *in vacuo* to yield an orange liquid (3.69 g, 85%). ^1H, ^{13}C NMR and MS^+ as for $[C_3(NPent_2)_3]Cl$. Found: C, 73.26; H,

11.58; N, 14.64%. Calc. for $C_{35}H_{66}N_5.0.16H_2O$: C, 73.26; H, 11.65; N, 14.65%. H_2O content: 316 ppm. Cl^- content: 312 ppm.

2.2.21 Tris(dihexylamino)cyclopropenium chloride, $[C_3(NHex_2)_3]Cl$

Dihexylamine (20.8 g, 112 mmol) and NEt_3 (45 mL, 323 mmol) was added to dichloromethane (200 mL) and cooled to 0 °C. C_3Cl_5H (4.84 g, 22.6 mmol) was added dropwise and the solution stirred overnight at ambient temperature. The solution was heated to reflux for 4 h, then washed with water (4 x 200 mL). Solution was acidified with aqueous HCl. The dichloromethane layer was separated and washed with water (4 x 200 mL). Removal of dichloromethane *in vacuo* yielded a viscous orange liquid (11.8 g, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.29 (t, $^3J_{HH}$ = 8.07 Hz, 12 H, NC*H*$_2$), 1.60 (m, 12 H, NCH$_2$C*H*$_2$), 1.28 (m, 36 H, NCH$_2$CH$_2$(C*H*$_2$)$_3$), 0.86 (t, $^3J_{HH}$ = 6.60 Hz, 18 H, N(CH$_2$)$_5$C*H*3). ^{13}C NMR (126 MHz, $CDCl_3$): 116.55 (C_3), 53.14 (N*C*H$_2$), 31.46 (NCH$_2$*C*H$_2$), 28.98 (N(CH$_2$)$_2$*C*H$_2$), 26.34 (N(CH$_2$)$_3$*C*H$_2$), 22.50 (N(CH$_2$)$_4$*C*H$_2$), 13.88 (N(CH$_2$)$_5$*C*H$_3$). ES^+ m/z as for $[C_3(NHex_2)_3]TFSA$.

2.2.22 Tris(dihexylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NHex_2)_3]TFSA$

$[C_3(NHex_2)_3]Cl$ (3.12 g, 5.00 mmol) was stirred with LiTFSA (4.0 g, 14.0 mmol) in water (50 mL). The product was extracted with dichloromethane (25 mL) and washed with water (50 mL). Additional LiTFSA (4.0 g, 14.0 mmol) and water (100 mL) was added. Added diethyl ether (100 mL), and washed the organic layer with water (4 x 100 mL) and dried *in vacuo* to yield an orange liquid (3.91 g, 90%). ^{1}H, ^{13}C NMR as for $[C_3(NHex_2)_3]Cl$. ES^+ m/z 588.6214 (100%, M^+). Found: C, 57.30; H, 9.22; N, 6.48%. Calc. for $C_{41}H_{78}N_4S_2O_4F_6$: C, 56.66; H, 9.04; N, 6.45%. H_2O content: 20 ppm. Cl^- content: 181 ppm.

2.2.23 Tris(dihexylamino)cyclopropenium dicyanamide, $[C_3(NHex_2)_3]DCA$

$[C_3(NHex_2)_3]Cl$ (3.85 g, 6.16 mmol) was stirred with NaDCA (2.5 g, 28.1 mmol) in water (50 mL). The product was extracted with dichloromethane (25 mL) and washed with

water (50 mL). Additional NaDCA (2.5 g, 28.1 mmol) and water (100 mL) was added. Extracted with diethyl ether (100 mL), washed with water (4 x 100 mL) and dried *in vacuo* to yield an orange liquid (3.61 g, 89%). ^{1}H, ^{13}C NMR and MS^{+} as for $[C_3(NHex_2)_3]Cl$. Found: C, 75.31; H, 12.25; N, 12.72%. Calc. for $C_{41}H_{78}N_6$: C, 75.17; H, 12.00; N, 12.83%. H_2O content: 272 ppm. Cl^- content: 1055 ppm.

2.2.24 Tris(dihexylamino)cyclopropenium dibutylphosphate, $[C_3(NHex_2)_3]DBP$

NaOH (2.56 g, 64.1 mmol) was dissolved in water (200 mL) and dibutylphosphate (12.4 mL, 62.5 mmol) was added. $[C_3(NHex_2)_3]Cl$ (6.44 g, 10.3 mmol) was stirred with half of the NaDBP solution for 30 min. The product was extracted with diethyl ether (200 mL), and diethyl ether solution was stirred with the remainder of the NaDBP solution for 30 min. The diethyl ether layer was separated and washed with water (3 x 100 mL). Diethyl ether solution was dried *in vacuo* to yield an orange liquid (7.64 g, 93%). ^{1}H, ^{13}C NMR and MS^{+} as for $[C_3(NHex_2)_3]Cl$. Found: C, 69.50; H, 12.27; N, 5.26%. Calc. for $C_{47}H_{96}N_3O_4P.0.77H_2O$: C, 69.50; H, 12.11; N, 5.17%. Cl^- content: 366 ppm.

2.2.25 Tris(didecylamino)cyclopropenium chloride, $[C_3(NDec_2)_3]Cl$

Didecylamine (13.8 g, 46.3 mmol) and NEt_3 (15 mL, 108 mmol) was added to dichloromethane (100 mL) and cooled to 0 °C. C_3Cl_5H (2.84 g, 13.2 mmol) was added dropwise and the solution stirred overnight at ambient temperature. The solution was heated to reflux for 6 h, then water added (200 mL). Solution was acidified with aqueous HCl, then separated and washed again with dilute aqueous HCl. The dichloromethane was separated and washed with water (3 x 150 mL). Removal of dichloromethane *in vacuo* yielded a viscous orange liquid and white precipitate. After addition of acetone and cooling in the freezer, precipitate was filtered through silica gel three times. Removal of acetone *in vacuo* yields an orange liquid (9.46 g, 74.5 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.26 (t, $^{3}J_{HH}$ = 7.70 Hz, 12H, NCH_2), 1.57 (m, 12H, NCH_2CH_2), 1.23 (m, 84H, $N(CH_2)_2(CH_2)_7$), 0.83 (t, $^{3}J_{HH}$ = 6.97 Hz, 18H, $N(CH_2)_9CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$): 116.49 (C_3), 53.11 (NCH_2), 31.78 (NCH_2CH_2), 29.50 ($N(CH_2)_2CH_2$), 29.44 ($N(CH_2)_3CH_2$), 29.34 ($N(CH_2)_4CH_2$), 29.21 ($N(CH_2)_5CH_2$), 29.01 ($N(CH_2)_6CH_2$), 26.66

($N(CH_2)_7CH_2$), 22.57 ($N(CH_2)_8CH_2$), 14.00 ($N(CH_2)_9CH_3$),. ES^+ m/z 924.9965 (100%, M^+). Found: C, 77.86; H, 13.23; N, 4.43%. Calc. for $C_{63}H_{126}N_3Cl.0.59H_2O$: C, 77.86; H, 13.19; N, 4.32%.

2.2.26 Tris(didecylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NDec_2)_3]TFSA$

$[C_3(NDec_2)_3]Cl$ (3.05 g, 3.18 mmol) was stirred with LiTFSA (4.0 g, 14.0 mmol). Water (100 mL) was added and product extracted with diethyl ether (200 mL). Additional LiTFSA (4.0 g, 14.0 mmol) and water (100 mL) was added. Diethyl ether solution was washed with water (3 x 100 mL) and dried *in vacuo* to yield an orange liquid (3.18 g, 83%). ^1H, ^{13}C NMR and MS^+ as for $[C_3(NDec_2)_3]Cl$. Found: C, 64.80; H, 10.57; N, 4.84%. Calc. for $C_{65}H_{126}N_4S_2O_4F_6$: C, 64.74; H, 10.53; N, 4.65%. H_2O content: 38 ppm. Cl^- content: 195 ppm.

2.2.27 Tris(didecylamino)cyclopropenium dicyanamide, $[C_3(NDec_2)_3]DCA$

$[C_3(NDec_2)_3]Cl$ (3.10 g, 3.23 mmol) was stirred with NaDCA (2.0 g, 22.5 mmol). Water (100 mL) was added and product extracted with diethyl ether (200 mL). Additional NaDCA (2.0 g, 22.5 mmol) and water (100 mL) was added. Diethyl ether solution was washed with water (3 x 100 mL) and dried *in vacuo* to yield an orange liquid (3.10 g, 97%). ^1H, ^{13}C NMR and MS^+ as for $[C_3(NDec_2)_3]Cl$. Found: C, 78.61; H, 12.88; N, 8.51%. Calc. for $C_{65}H_{126}N_4S_2O_4F_6$: C, 78.72; H, 12.81; N, 8.47%. H_2O content: 186 ppm. Cl^- content: 369 ppm.

2.2.28 Tris(diallylamino)cyclopropenium chloride, $[C_3(NAllyl_2)_3]Cl$

C_3Cl_5H (6.67 g, 31.1 mmol) was dissolved in dichloromethane (100 mL) and cooled to 0 °C. $HNAllyl_2$ (23.6 g, 243 mmol) was added dropwise and the solution stirred overnight at ambient temperature. The solution was heated to reflux for 4 h, before dichloromethane and excess amine was removed *in vacuo*. $[H_2NAllyl_2]Cl$ was removed by dissolving in chloroform (100 mL) and washing with water (3 x 100 mL). Removal of chloroform *in vacuo* yielded a yellow liquid (9.95 g, 89% yield). ^1H NMR (500 MHz,

$CDCl_3$): 5.58 (m, 6H, NCH_2CHCH_2), 5.04 (m, 12H, NCH_2CHCH_2), 3.76 (d, $^3J_{HH}$ = 5.14 Hz, 13H, NCH_2CHCH_2). ^{13}C NMR (126 MHz, $CDCl_3$): 130.81 (NCH_2CHCH_2), 118.39 (NCH_2CHCH_2), 116.36 (C_3), 54.03 (NCH_2CHCH_2). ES^+ m/z 324 (100%, M^+). Found: C, 67.22; H, 8.51; N, 10.82; Cl, 9.17%. Calc. for $C_{21}H_{30}N_3Cl.0.85H_2O$: C, 67.22; H, 8.51; N, 11.20; Cl, 9.45%.

2.2.29 Tris(diallylamino)cyclopropenium bromide, $[C_3(NAllyl_2)_3]Br$

$[C_3(NAllyl_2)_3]Cl$ (1.07 g, 2.98 mmol) was stirred with HBr (7 mL, 38%, 44 mmol). The product was extracted with dichloromethane (2 x 25 mL), washed twice more with HBr (5 mL, 38%, 33 mmol), washed with water (4 x 50 mL) until the pH was neutral, and then dried *in vacuo* to yield a dark brown solid (0.8 g, 67%). ^1H, ^{13}C NMR and MS^+ as for $[C_3(NAllyl_2)_3]Cl$. Found: C, 61.47; H, 7.58; N, 9.81%. Calc. for $C_{21}H_{30}N_3Br.0.33H_2O$: C, 61.47; H, 7.53; N, 10.24%.

2.2.30 Tris(butylmethylamino)cyclopropenium chloride, $[C_3(NBuMe)_3]Cl$

HNBuMe (81.0 g, 929 mmol) was added to dichloromethane (250 mL) and cooled to 0 °C. C_3Cl_5H (25.0 g, 117 mmol) was added dropwise and the solution stirred overnight at ambient temperature. The solution was heated to reflux for 5 h, before dichloromethane and excess amine was removed *in vacuo*. Acetone (200 mL) was added and the $[H_2NBuMe]Cl$ precipitate was filtered off. Acetone was removed *in vacuo*. The crude product was dissolved in water (500 mL), washed with diethyl ether (2 x 100mL) and pet ether (2 x 75 mL) to remove residual amine, followed by extraction with chloroform (4 x 100 mL). Removal of chloroform *in vacuo* gave a light yellow liquid (35.0 g, 91% yield). ^1H NMR (500 MHz, $CDCl_3$): 3.29 (t, $^3J_{HH}$ = 7.8 Hz, 6H, NCH_2), 3.12 (s, 9H, NCH_3), 1.56 (m, 6H, NCH_2CH_2), 1.27 (m, 6H, $NCH_2CH_2CH_2$), 0.88 (t, $^3J_{HH}$ = 7.5 Hz, 9H, $N(CH_2)_3CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$): 116.75 (C_3), 55.32 (NCH_2), 40.18 (NCH_3), 29.89 (NCH_2CH_2), 19.71 ($NCH_2CH_2CH_2$), 13.64 (CH_2CH_3). ES^+ m/z 294.2921 (100%, M^+) Found: C, 61.32; H, 10.94; N, 11.99%. Calc. for $C_{18}H_{36}N_3Cl.1.26H_2O$: C, 61.32; H, 11.01; N, 11.92%.

2.2.31 Tris(butylmethylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NBuMe)_3]TFSA$

$[C_3(NBuMe)_3]Cl$ (3.00 g, 9.10 mmol) was stirred with LiTFSA (5.00 g, 17.4 mmol) in water (100 mL). The product was extracted with chloroform (50 mL) washed with water (3 x 50 mL) and was dried *in vacuo* to yield a yellow liquid (3.90 g, 75%). ^1H, ^{13}C NMR and MS^+ as for $[C_3(NBuMe)_3]Cl$. Found: C, 41.52; H, 6.30; N, 9.88%. Calc. for $C_{20}H_{36}N_4S_2O_4F_6$: C, 41.80; H, 6.31; N, 9.75%. H_2O content: 188 ppm. Cl^- content: 343 ppm.

2.2.32 Tris(butylmethylamino)cyclopropenium dicyanamide, $[C_3(NBuMe)_3]DCA$

$[C_3(NBuMe)_3]Cl$ (5.30 g, 16.1 mmol) was stirred with NaDCA (3.65 g, 41.0 mmol) in water (100 mL). The product was extracted with chloroform (50 mL) washed with water (3 x 50 mL)) and dried *in vacuo* to yield a yellow liquid (5.40 g, 93%). ^1H, ^{13}C NMR and MS^+ as for $[C_3(NBuMe)_3]Cl$ with an additional peak due to DCA. Found: C, 66.33; H, 10.27; N, 23.19%. Calc. for $C_{20}H_{36}N_6$: C, 66.63; H, 10.06; N, 23.31%. H_2O content: 1139 ppm. Cl^- content: 156 ppm.

2.2.33 Tris(octadecylmethylamino)cyclopropenium chloride, $[C_3(NC_{18}Me)_3]Cl$

Methyloctadecylamine (11.6 g, 40.9 mmol) and NEt_3 (15 mL, 108 mmol) was added to dichloromethane (75 mL) and cooled to 0 °C. C_3Cl_5H (2.92 g, 13.6 mmol) was added dropwise and the solution stirred for 60 h at ambient temperature. The solution was heated to reflux for 20 h, then dichloromethane was removed *in vacuo*. Chloroform (200 mL) added and washed with water (3 x 100 mL). Chloroform was removed *in vacuo*, and the crude, solid product was washed with pet ether, leaving a pale yellow solid (10.2 g, 81% yield). ^1H NMR (300 MHz, $CDCl_3$): 3.33 (t, $^3J_{HH}$ = 7.6 Hz, 6H, $NCH_2C_{17}H_{35}$), 3.17 (s, 9H, NCH_3), 1.60 (m, 6H, $NCH_2CH_2C_{16}H_{33}$), 1.12–34 (m, 90H, $NC_2H_4C_{15}H_{30}CH_3$), 0.85 (t, $^3J_{HH}$ = 6.5 Hz, 9H, $NC_{17}H_{34}CH_3$). ^{13}C NMR (75 MHz, $CDCl_3$): 116.99 (C_3), 55.70 (NCH_2), 40.31 (NCH_3), 31.90, 28.72–30.42, 28.05, 26.66, 22.66, 14.10 (CH_3). ES^+ m/z 882.9465 (100%, M^+). Found: C, 75.18; H, 12.86; N, 4.56%. Calc. for $C_{60}H_{120}N_3Cl.2.19H_2O$: C, 75.18; H, 13.08; N, 4.38%.

2.2.34 Tris(octadecylmethylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NC_{18}Me)_3]TFSA$

$[C_3(NC_{18}Me)_3]Cl$ (4.00 g, 4.35 mmol) was stirred with LiTFSA (5.00 g, 17.4 mmol) in water (100 mL). The product was extracted with chloroform (100 mL), washed with water (3 x 50 mL) and dried *in vacuo* to yield a yellow solid (4.30 g, 85%). ^1H, ^{13}C NMR and MS^+ as for $[C_3(NC_{18}Me)_3]Cl$. Found: C, 62.54; H, 10.24; N, 4.87%. Calc. for $C_{62}H_{120}N_4S_2O_4F_6.1.50H_2O$: C, 62.54; H, 10.41; N, 4.71%.

2.2.35 Tris(octadecylmethylamino)cyclopropenium dicyanamide, $[C_3(NC_{18}Me)_3]DCA$

$[C_3(NC_{18}Me)_3]Cl$ (4.00 g, 4.35 mmol) was stirred with NaDCA (1.2 g, 13.5 mmol) in water (100 mL). The product was extracted with dichloromethane (100 mL), washed with water (3 x 100 mL) and dried *in vacuo* to yield a yellow solid (3.30 g, 80%). ^1H, ^{13}C NMR and MS^+ as for $[C_3(NC_{18}Me)_3]Cl$. Found: C, 77.31; H, 12.90; N, 9.10%. Calc. for $C_{62}H_{120}N_60.75H_2O$: C, 11.31; H, 12.71; N, 8.72%.

2.2.36 Bis(diethylamino)dimethylaminocyclopropenium methylsulfate, $[C_3(NEt_2)_2NMe_2]MeSO_4$

Cyclopropenone $(Et_2N)_2C_3O$ (8.91 g, 45.5 mmol) was dried, then Me_2SO_4 (8.60 g, 68.2 mmol) was added and stirred at ambient temperature for 30 mins. The mixture was cooled to –72 °C, then $HNMe_2$ (6.80 g, 150 mmol) was added and stirred for 1 h, then gradually allowed to warm to ambient temperature overnight. Dissolved in chloroform (100 mL), extracted with water (2 x 125 mL) and washed with dichloromethane (2 x 75 mL). The product was extracted with chloroform (2 x 75 mL) and chloroform removed *in vacuo*, yielding a yellow liquid (5.72 g, 38%). $[C_3(NEt_2)_2NMe_2]^+$ (12.7 mmol, 28%) was recovered from the dichloromethane and water washings by converting to the TFSA anion. ^1H NMR (300 MHz, $CDCl_3$) δ ppm 3.68 (s, 3H, CH_3SO_4), 3.40 (q, $^3J_{HH}$ = 7.3 Hz, 8H, NCH_2CH_3), 3.17 (s, 6H, NCH_3), 1.27 (t, $^3J_{HH}$ = 7.2 Hz, 12H, NCH_2CH_3). ^{13}C NMR (126 MHz, $CDCl_3$): 117.83 (C_1), 116.31 (C_2), 54.02 (CH_3SO_4), 47.28 (NCH_2CH_3), 42.07 (CH_3), 14.07 (NCH_2CH_3). ES^+ m/z 224.2122 (100%, M^+).

2.2.37 Bis(diethylamino)dimethylaminocyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2NMe_2]TFSA$

Dichloromethane washings from the synthesis of $[C_3(NEt_2)_2NMe_2]MeSO_4$ had the solvent removed *in vacuo* and were then combined with $[C_3(NEt_2)_2NMe_2]MeSO_4$ (1.50 g, 4.48 mmol) and stirred with LiTFSA (18 g, 62.9 mmol). Diethyl ether (200 mL) was added, washed with water (4 x 200 mL) and dried *in vacuo* to yield a yellow liquid (2.63 g, 5.21 mmol). Water washings from the synthesis of $[C_3(NEt_2)_2NMe_2]MeSO_4$ were dried *in vacuo* and stirred with LiTFSA (20 g, 69.9 mmol). Diethyl ether (300 mL) was added, washed with water (4 x 300 mL) and dried *in vacuo* to yield a yellow liquid (6.04 g, 12.0 mmol). Samples of $[C_3(NEt_2)_2NMe_2]TFSA$ were then combined. ^1H, ^{13}C NMR and MS^+ as for $[C_3(NEt_2)_2NMe_2]MeSO_4$. Found: C, 35.96; H, 5.29; N, 11.07%. Calc. for $C_{15}H_{26}N_4S_2O_4F_6$: C, 35.71; H, 5.19; N, 11.11%. H_2O content: 142 ppm. Cl^- content: 62 ppm.

2.2.38 Bis(diethylamino)dimethylaminocyclopropenium dicyanamide, $[C_3(NEt_2)_2NMe_2]DCA$

$[C_3(NEt_2)_2NMe_2]MeSO_4$ (4.34 g, 13.0 mmol) was stirred with NaDCA (5.60 g, 62.9 mmol). Added chloroform (100 mL), washed with water (3 x 100 mL) and dried *in vacuo* to yield a yellow liquid (3.24 g, 86%). ^1H, ^{13}C NMR and MS^+ as for $[C_3(NEt_2)_2NMe_2]MeSO_4$. Found: C, 58.91; H, 8.90; N, 26.66%. Calc. for $C_{15}H_{26}N_60.86H_2O$: C, 58.91; H, 9.13; N, 27.48%. H_2O content: 1115 ppm. Cl^- content: 3554 ppm.

2.2.39 Bis(diethylamino)dibutylaminocyclopropenium methylsulfate, $[C_3(NEt_2)_2NBu_2]MeSO_4$

Cyclopropenone $(Et_2N)_2C_3O$ (6.23 g, 31.8 mmol) was dried, then Me_2SO_4 (4.40 g, 34.9 mmol) was added and stirred at ambient temperature for 20 mins. HN^nBu_2 (4.91 g, 38.0 mmol) was added and stirred for 20 mins. The mixture was washed with pentane (3 x 75 mL), dissolved into water (150 mL), extracted into chloroform (2 x 100 mL) and washed with water (2 x 100 mL). Chloroform was removed *in vacuo* and crude product washed with diethyl ether (4 x 75 mL), which gave a dark orange liquid (6.31 g, 47%). ^1H NMR

(300 MHz, $CDCl_3$): 3.69 (s, 3H, CH_3SO_4), 3.40 (q, $^3J_{HH}$ = 7.1 Hz, 8H, NCH_2CH_3), 3.28 (t, $^3J_{HH}$ = 7.91 Hz, 4H, NCH_2CH_2), 1.60 (m, 4H, NCH_2CH_2), 1.19–39 (m, 16H, $NCH_2CH_2CH_2$ and NCH_2CH_3), 0.93 (t, $^3J_{HH}$ = 7.33 Hz, 6H, $CH_2CH_2CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$): 116.76 (C_1), 116.64 (C_2), 54.35 (CH_3SO_4), 53.17 (NCH_2CH_2), 47.35 (NCH_2CH_3), 31.28 (NCH_2CH_2), 20.10 ($NCH_2CH_2CH_2$), 14.54 (NCH_2CH_3), 14.00 ($CH_2CH_2CH_3$). ES^+ m/z 308.3054 (100%, M^+).

2.2.40 Bis(diethylamino)dibutylaminocyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2NBu_2]TFSA$

$[C_3(NEt_2)_2NBu_2]MeSO_4$ (7.35 g, 17.5 mmol) was stirred with LiTFSA (10.0 g, 34.8 mmol) in water (150 mL). The product was extracted with chloroform (150 mL), washed with water (3 x 150 mL) and dried *in vacuo* to yield a dark orange liquid (6.71 g, 65%). ^1H, ^{13}C NMR and MS^+ as for $[C_3(NEt_2)_2NBu_2]MeSO_4$. Found: C, 42.95; H, 6.72; N, 9.60; F, 19.42; S, 10.79%. Calc. for $C_{21}H_{38}N_4S_2O_4F_6$: C, 42.85; H, 6.51; N, 9.52; F, 19.36; S, 10.89%. H_2O content: 57 ppm. Cl^- content: 83 ppm.

2.2.41 Bis(diethylamino)dibutylaminocyclopropenium dicyanamide, $[C_3(NEt_2)_2NBu_2]DCA$

$[C_3(NEt_2)_2NBu_2]MeSO_4$ (6.31 g, 15.0 mmol) was stirred with NaDCA (4.00 g, 44.9 mmol) in water (150 mL). The product was extracted with chloroform (150 mL), washed with water (3 x 150 mL) and dried *in vacuo* to yield a dark orange liquid (5.05 g, 90%). ^1H, ^{13}C NMR and MS^+ as for $[C_3(NEt_2)_2NBu_2]MeSO_4$ with an additional peak due to DCA. Found: C, 64.93; H, 9.68; N, 21.85%. Calc. for $C_{21}H_{38}N_6.0.77H_2O$: C, 64.93; H, 10.26; N, 21.63%. H_2O content: 624 ppm. Cl^- content: 263 ppm.

2.2.42 Bis(diethylamino)dihexylaminocyclopropenium methylsulfate, $[C_3(NEt_2)_2NHex_2]MeSO_4$

Cyclopropenone $(Et_2N)_2C_3O$ (5.53 g, 28.2 mmol) was dried, then Me_2SO_4 (5.33 g, 42.3 mmol) was added and stirred at ambient temperature for 30 mins. HN^nHex_2 (9.03 g, 48.7 mmol) was added and stirred overnight. The mixture was washed with pet ether (3 x 50 mL), dissolved into water (150 mL), extracted into chloroform (150 mL) and washed

with water (3 x 100 mL). Chloroform was removed *in vacuo* and dilute NaOH was added, which was washed with pentane (3 x 100 mL) and neutralized with aqueous HCl. The product was extracted with chloroform (150 mL) and washed with water (3 x 100 mL). Removal of chloroform *in vacuo* yielded an orange liquid (10.9 g, 81%). ^{1}H NMR (300 MHz, $CDCl_3$): 3.69 (s, 3H, C*H*$_3$MeSO$_4$), 3.41 (q, $^{3}J_{HH}$ = 7.3 Hz, 8H, NC*H*$_2$CH$_3$), 3.27 (t, $^{3}J_{HH}$ = 8.5 Hz, 4H, NC*H*$_2$C$_5$H$_{11}$), 1.60 (m, 4H, NCH$_2$C*H*$_2$C$_4$H$_9$), 1.19–35 (m, 24H, N(CH$_2$)$_2$(C*H*$_2$)$_3$CH$_3$ and NCH$_2$C*H*$_3$), 0.86 (t, $^{3}J_{HH}$ = 6.5 Hz, 6H, N(C$_5$H$_{10}$)C*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): 116.45 (C_1), 116.38 (C_2), 54.26 (CH_3SO_4), 53.17 (N*C*H$_2$C$_5$H$_{11}$), 47.10 (N*C*H$_2$CH$_3$), 31.39 (NCH$_2$*C*H$_2$C$_4$H$_9$), 29.02 (NC$_2$H$_4$*C*H$_2$C$_3$H$_7$), 26.25 (NC$_3$H$_6$*C*H$_2$C$_2$H$_5$), 22.47 (NC$_4$H$_8$*C*H$_2$CH$_3$), 14.29 (NCH$_2$*C*H$_3$), 13.91 (NC$_5$H$_{10}$*C*H$_3$). ES$^+$ m/z as for [C$_3$(NEt$_2$)$_2$NHex$_2$]TFSA.

2.2.43 Bis(diethylamino)dihexylaminocyclopropenium bis(trifluoromethanesulfonyl)amide, [C$_3$(NEt$_2$)$_2$NHex$_2$]TFSA

[C$_3$(NEt$_2$)$_2$NHex$_2$]I samples contaminated with (Et$_2$N)$_2$C$_3$O were combined and a large excess of LiTFSA (20 g, 69.7 mmol) in water (300 mL) was added. The product was extracted with chloroform (300 mL) and washed with water (2 x 300 mL). (Et$_2$N)$_2$C$_3$O was removed by washing with petroleum ether/diethylether mixture (1:1, 3 x 100 mL) and was dried *in vacuo* to yield a dark brown liquid (4 g). ^{1}H, ^{13}C NMR as for [C$_3$(NEt$_2$)$_2$NHex$_2$]MeSO$_4$. ES$^+$ m/z 364.3680 (100%, M$^+$). Found: C, 47.35; H, 7.58; N, 8.78; F, 14.87%. Calc. for C$_{25}$H$_{46}$N$_4$S$_2$O$_4$F$_6$: C, 46.57; H, 7.19; N, 8.69; F, 17.68%. H$_2$O content: 76 ppm.

2.2.44 Bis(diethylamino)dihexylaminocyclopropenium dicyanamide, [C$_3$(NEt$_2$)$_2$NHex$_2$]DCA

[C$_3$(NEt$_2$)$_2$NHex$_2$]MeSO$_4$ (10.9 g, 22.9 mmol) was stirred with NaDCA (7.50 g, 84.2 mmol) in water (150 mL). The product was extracted with chloroform (150 mL), washed with water (4 x 100 mL) and dried *in vacuo* to yield an orange liquid (8.86 g, 90%). ^{1}H, ^{13}C NMR as for cation of [C$_3$(NEt$_2$)$_2$NHex$_2$]MeSO$_4$. ES$^+$ m/z as for [C$_3$(NEt$_2$)$_2$NHex$_2$]TFSA. Found: C, 67.43; H, 10.62; N, 18.71%. Calc. for

$C_{25}H_{46}N_6.0.81H_2O$: C, 67.43; H, 10.78; N, 18.87%. H_2O content: 894 ppm. Cl^- content: 519 ppm.

2.2.45 Bis(diethylamino)butylmethylaminocyclopropenium methylsulfate, $[C_3(NEt_2)_2NBuMe]MeSO_4$

Cyclopropenone $(Et_2N)_2C_3O$ (6.41 g, 32.7 mmol) was dried, then Me_2SO_4 (8.26 g, 65.5 mmol) was added and stirred at ambient temperature for 30 mins. HN^nBuMe (7.14 g, 81.9 mmol) was added and stirred for 1 h. Water (100 mL) was added and washed with pet ether (3 x 100 mL), extracted into chloroform (2 x 100 mL) and washed with water (100 mL). Chloroform was removed *in vacuo*, and the crude product was washed with diethyl ether (5 x 50 mL), yielding an orange liquid (9.70 g, 79%). ^{1}H NMR (300 MHz, $CDCl_3$): 3.66 (s, 3H, C*H*$_3$SO$_4$), 3.39 (q, $^3J_{HH}$ = 7.3 Hz, 8H, NC*H*$_2$CH$_3$), 3.30 (t, $^3J_{HH}$ = 7.9 Hz, 2H, NC*H*$_2$CH$_2$), 3.13 (s, 3H, NC*H*$_3$), 1.59 (m, 2H, NCH$_2$C*H*$_2$), 1.19–38 (m, 14H, NCH$_2$CH$_2$C*H*$_2$ and NCH$_2$C*H*$_3$), 0.92 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH$_2$C*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$): 117.20 (C_1), 116.14 (C_2), 55.16 (N*C*H$_2$CH$_2$), 54.04 (CH_3SO_4), 47.18 (N*C*H$_2$CH$_3$), 39.53 (N*C*H$_3$), 30.01 (NCH$_2$*C*H$_2$), 19.72 (NCH$_2$CH$_2$*C*H$_2$), 14.14 (NCH$_2$*C*H$_3$), 13.68 (CH$_2$CH$_2$*C*H$_3$). ES^+ m/z 266.2583 (100%, M^+).

2.2.46 Bis(diethylamino)butylmethylaminocyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2NBuMe]TFSA$

$[C_3(NEt_2)_2NBuMe]MeSO_4$ (3.90 g, 10.3 mmol) was stirred with LiTFSA (10 g, 34.8 mmol) in water (100 mL). The product was extracted with chloroform (150 mL), washed with water (3 x 100 mL) and dried *in vacuo* to yield an orange liquid (4.48 g, 79%). ^{1}H, ^{13}C NMR and MS^+ as for $[C_3(NEt_2)_2NBuMe]MeSO_4$. Found: C, 40.07; H, 5.93; N, 10.13%. Calc. for $C_{18}H_{32}N_4S_2O_4F_6$: C, 39.55; H, 5.90; N, 10.25%. H_2O content: 407 ppm. Cl^- content: 97 ppm.

2.2.47 Bis(diethylamino)butylmethylaminocyclopropenium dicyanamide, $[C_3(NEt_2)_2NBuMe]DCA$

$[C_3(NEt_2)_2NBuMe]MeSO_4$ (5.50 g, 14.6 mmol) was stirred with NaDCA (4.00 g, 44.9 mmol) in water (100 mL). The product was extracted with chloroform (100 mL), washed

with water (3 x 100 mL) and dried *in vacuo* to yield an orange liquid (4.10 g, 85%). ^{1}H, ^{13}C NMR and MS^{+} as for $[C_3(NEt_2)_2NBuMe]MeSO_4$ with an additional peak due to DCA. Found: C, 63.08; H, 9.86; N, 24.78%. Calc. for $C_{18}H_{32}N_6$: C, 63.31; H, 9.74; N, 24.61%. H_2O content: 1043 ppm. Cl^- content: 202 ppm.

2.2.48 Bis(diethylamino)hexylmethylaminocyclopropenium methylsulfate, $[C_3(NEt_2)_2NHexMe]MeSO_4$

Cyclopropenone $(Et_2N)_2C_3O$ (5.87 g, 29.9 mmol) and dimethylsulfate (5.67 g, 44.9 mmol) were mixed at ambient temperature overnight. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.24 (s, $(CH_3)_2SO_4$), 3.95 (s, OCH_3), 3.68 (s, CH_3SO_4), 3.46 (q, $^{3}J_{HH}$ = 7.2 Hz, NCH_2CH_3), 1.30 (t, $^{3}J_{HH}$ = 7.2 Hz, NCH_2CH_3). Hexylmethylamine (5.34 g, 46.4 mmol) added and the solution stirred at ambient temperature for 1 h. ^{1}H NMR showed a ratio of 17.88 $[C_3(NEt_2)_2NBuMe]^+$: 1 $(Et_2N)_2C_3O$. The product was washed with pet ether (5 x 40 mL). The product was then dissolved in water (100 mL), extracted with dichloromethane (2 x 100 mL) and washed with water (2 x 100 mL). Dichloromethane was removed *in vacuo*, and the crude product then washed with diethyl ether (6 x 50 mL), to give an orange liquid (9.178 g, 78%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.67 (s, 3H, CH_3SO_4), 3.40 (q, $^{3}J_{HH}$ = 7.2 Hz, NCH_2CH_3), 3.30 (t, $^{3}J_{HH}$ = 7.8 Hz, $NCH_2(CH_2)_4CH_3$), 3.14 (s, NCH_3), 1.62 (m, $NCH_2CH_2(CH_2)_3CH_3$), 1.19–36 (m, NCH_2CH_3 and $N(CH_2)_2(CH_2)_3CH_3$), 0.85 (t, $^{3}J_{HH}$ = 6.9 Hz, $NCH_2(CH_2)_4CH_3$). ^{13}C NMR and MS^{+} as for $[C_3(NEt_2)_2NHexMe]$TFSA.

2.2.49 Bis(diethylamino)hexylmethylaminocyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2NHexMe]$TFSA

$[C_3(NEt_2)_2NHexMe]MeSO_4$ (3.33 g, 8.22 mmol) was stirred with LiTFSA (8.73 g, 30.5 mmol) in water (200 mL). The product was extracted with dichloromethane/diethyl ether mixture (1:1, 200 mL) and dichloromethane (50 mL). More LiTFSA (5.04 g, 17.6 mmol) and water (200 mL) was added and stirred. The organic layer was washed with water (3 x 100 mL) and dried *in vacuo* to yield an orange liquid (4.60 g, 98%). ^{1}H NMR as for cation of $[C_3(NEt_2)_2NHexMe]MeSO_4$. ^{13}C NMR (75 MHz, $CDCl_3$): 120.21 (q, $^{3}J_{CF}$ = 322.18 Hz, CF_3) 117.36 (C_1), 116.40 (C_2), 55.73 ($NCH_2C_5H_{11}$), 47.39 (NCH_2CH_3), 39.66 (NCH_3), 31.63 ($NCH_2CH_2C_4H_9$), 28.21 ($N(C_2H_4)CH_2C_3H_7$), 26.45 ($NC_3H_6CH_2C_2H_5$),

22.72 ($NC_4H_8CH_2CH_3$), 14.25 (NCH_2CH_3), 14.16 ($NC_5H_{10}CH_3$). ES^+ m/z 294.2903 (100%, M^+). Found: C, 42.78; H, 6.35; N, 9.75%. Calc. for $C_{20}H_{36}N_4S_2O_4F_6$: C, 41.80; H, 6.31; N, 9.75%. H_2O content: 82 ppm. Cl^- content: 103 ppm.

2.2.50 Bis(diethylamino)hexylmethylaminocyclopropenium dicyanamide, $[C_3(NEt_2)_2NHexMe]DCA$

$[C_3(NEt_2)_2NHexMe]MeSO_4$ (5.42 g, 13.4 mmol) was stirred with NaDCA (4.37 g, 49.1 mmol) in water (200 mL). The product was extracted with dichloromethane (150 mL), and additional NaDCA (3.22 g, 36.2 mmol) in water (200 mL) added. The dichloromethane layer was washed with water (3 x 100 mL) and dried *in vacuo* to yield an orange liquid (4.20 g, 87%). ^1H NMR as for cation of $[C_3(NEt_2)_2NHexMe]MeSO_4$, ^{13}C NMR and MS^+ as for cation of $[C_3(NEt_2)_2NHexMe]TFSA$. Found: C, 65.86; H, 10.09; N, 22.81%. Calc. for $C_{20}H_{36}N_6.0.23H_2O$: C, 65.86; H, 10.08; N, 23.04%. H_2O content: 604 ppm. Cl^- content: 619 ppm. $[C_3(NEt_2)_2NHexH]$

2.2.51 Bis(diethylamino)hexylaminocyclopropenium chloride, $[C_3(NEt_2)_2NHexH]Cl$

Dried cyclopropenone $(Et_2N)_2C_3O$ (4.61 g, 23.5 mmol) and dimethylsulfate (5.93 g, 47.0 mmol) were mixed at ambient temperature for 1h. Hexylamine (15.32 g, 151 mmol) added and the solution stirred at ambient temperature for 3 h. The product was washed with a diethyl ether pet ether mixture (3 x 75 mL, 1:1 ratio). The product was then dissolved in water (50 mL), acidified with HCl acid, extracted with dichloromethane (50 mL) and washed with water (3 x 75 mL). Dichloromethane was removed *in vacuo*, then washed with diethyl ether (4 x 50 mL). Aqueous NaOH (200 mL, 0.38 $molL^{-1}$) added, and washed with pet ether (4 x 100 mL) and diethyl ether (3 x 100 mL). Acidified with HCl and water removed *in vacuo*. Addition of acetone causes precipitation of NaCl, which was filtered off. Removal of acetone *in vacuo* yields a yellow liquid (2.64 g, 34%) of the mostly chloride salt, with a small amount of methylsulfate anions. ^1H NMR (500 MHz, $CDCl_3$): δ 9.04 (br. s, 1H, N*H*), 3.69 (s, (CH_3)SO_4), 3.39 (br. q, $^3J_{HH}$ = 7.0 Hz, NCH_2CH_3), 3.19 (q, $^3J_{HH}$ = 7.0 Hz, $NCH_2(CH_2)_4CH_3$), 1.65 (m, $NCH_2CH_2(CH_2)_3CH_3$), 1.18–35 (m, NCH_2CH_3 and $N(CH_2)_2(CH_2)_3CH_3$), 0.82 (t, $^3J_{HH}$ = 6.8 Hz,

$NCH_2(CH_2)_4CH_3$). ^{13}C NMR (125 MHz, $CDCl_3$): 116.93 (C_1 and C_2), 54.61 (CH_3SO_4), 47.64 ($NCH_2C_5H_{11}$), 46.82 (NCH_2CH_3), 31.65 ($NCH_2CH_2C_4H_9$), 30.67 ($N(C_2H_4)CH_2C_3H_7$), 26.69 ($NC_3H_6CH_2C_2H_5$), 22.74 ($NC_4H_8CH_2CH_3$), 14.53 (NCH_2CH_3), 14.123($NC_5H_{10}CH_3$). MS^+ as for $[C_3(NEt_2)_2NHexH]TFSA$.

2.2.52 Bis(diethylamino)hexylaminocyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2NHexH]TFSA$

$[C_3(NEt_2)_2NHexMe]Cl$ (2.64 g, 7.97 mmol) from above was stirred with LiTFSA (6.9 g, 24.1 mmol) in water (200 mL) for 30 min. The product was extracted with diethyl ether (200 mL). More LiTFSA (6.3 g, 22.0 mmol) and water (200 mL) was added and stirred for 1.5 h. Organic layer was washed with water (4 x 75 mL) and dried *in vacuo* to yield a yellow liquid (3.50 g, 78%). ^1H NMR and ^{13}C NMR as for $[C_3(NEt_2)_2NHexH]^+$. ES^+ m/z 280.2749 (100%, M^+). Found: C, 41.43; H, 6.11; N, 10.07%. Calc. for $C_{17}H_{34}N_4S_2O_4F_6$: C, 40.71; H, 6.11; N, 9.99%. H_2O content: 145 ppm. Cl^- content: 426 ppm.

2.2.53 Bis(diethylamino)diethanolaminocyclopropenium iodide, $[C_3(NEt_2)_2N(C_2H_4OH)_2]I$

Cyclopropenone $(Et_2N)_2C_3O$ (7.68 g, 39.2 mmol) was dried using ethanol azeotropes (5 x 50 mL). Iodoethane (97.5 g, 625 mmol) was added and heated to reflux for 18 h. Cooled to ambient temperature and $HN(C_2H_4OH)_2$ (8.44 g, 80.3 mmol) added. Continued stirring at ambient temperature 48 h. Excess iodoethane was removed *in vacuo* and water (100 mL) added. Extracted cyclopropenone with dichloromethane (100 mL, 50 mL), then extracted product from dichloromethane with water (2 x 100 mL) and water was recombined with previous water layer. Extracted product with dichloromethane (3 x 100 mL), yielding a yellow liquid (3.50 g, 22%). ^1H NMR (300 MHz, D_2O): 3.73 (t, $^3J_{HH}$ = 5.27 Hz, 4H, NCH_2CH_2OH), 3.47 (t, $^3J_{HH}$ = 5.27 Hz, 4H, NCH_2CH_2OH), 3.37 (q, $^3J_{HH}$ = 7.03 Hz, 8H, NCH_2CH_3), 1.17 (t, $^3J_{HH}$ = 7.18 Hz, 12H, NCH_2CH_3). ^{13}C NMR (75 MHz, D_2O, methanol reference): 117.89 (C_1), 117.26 (C_2), 59.46 (NCH_2CH_2OH), 54.38 (NCH_2CH_2OH), 47.20 (NCH_2CH_3), 13.98 (NCH_2CH_3).

2.2.54 Bis(diethylamino)diethanolaminocyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2N(C_2H_4OH)_2]TFSA$

$[C_3(NEt_2)_2N(C_2H_4OH)_2]I$ (3.50 g, 8.52 mmol) was stirred with LiTFSA (5.0 g, 17 mmol) in water (150 mL). The product was extracted with chloroform (150 mL), washed with water (4 x 150 mL) and dried *in vacuo* to yield a yellow liquid (3.5 g, 73%). ^1H and ^{13}C NMR as for $[C_3(NEt_2)_2N(C_2H_4OH)_2]I$ with an additional peak at 119.8 in the ^{13}C-NMR spectrum due to TFSA. ES^+ m/z 284.2344 (100%, M^+). Found: C, 36.45; H, 5.24; N, 9.86%. Calc. for $C_{17}H_{30}N_4S_2O_6F_6$: C, 36.17; H, 5.36; N, 9.92%.

2.2.55 Bis(diethylamino)diethanolaminocyclopropenium methylsulfate, $[C_3(NEt_2)_2N(C_2H_4OH)_2]MeSO_4$

Cyclopropenone $(Et_2N)_2C_3O$ (8.88 g, 45.3 mmol) was dried, then Me_2SO_4 (8.53 g, 67.6 mmol) was added and stirred at ambient temperature for 30 mins. $HN(C_2H_4OH)_2$ (8.10 g, 77.0 mmol) was added and stirred for 1 h. Dissolved into water (75 mL), and extracted cyclopropenone and $[C_3(NEt_2)_2N(C_2H_4OH)_2]MeSO_4$ with dichloromethane (8 x 75 mL). $[C_3(NEt_2)_2N(C_2H_4OH)_2]MeSO_4$ was then extracted using water (3 x 50 mL). Drying *in vacuo* yielded a yellow liquid (6.40 g, 36%). ^1H NMR (500 MHz, $CDCl_3$): 4.78 (s, O*H*), 3.82 (t, $^3J_{HH}$ = 4.77 Hz, 4H, NCH_2CH_2OH), 3.66 (s, 2.7H, CH_3SO_4), 3.51 (t, $^3J_{HH}$ = 4.95 Hz, 4H, NCH_2CH_2OH), 3.42 (q, $^3J_{HH}$ = 7.09 Hz, 8H, NCH_2CH_3), 1.25 (t, $^3J_{HH}$ = 7.15 Hz, 12H, NCH_2CH_3). ^{13}C NMR as for cation of $[C_3(NEt_2)_2N(C_2H_4OH)_2]I$.

2.2.56 Tris(diethanolamino)cyclopropenium chloride, $[C_3(N(C_2H_4OH)_2)_3]Cl$

$HN(C_2H_4OH)_2$ (97.1 g, 0.925 mol) was mixed with dichloromethane (250 mL), and the suspension was cooled to 0 °C. C_3Cl_5H (24.7 g, 0.115 mol) was added dropwise and the solution stirred overnight. The mixture was heated to reflux for 24 h. Dichloromethane was then removed *in vacuo*. The mixture was dissolved into ethanol (150 mL) and molecular sieves (13X, 10 Å pore size) were added slowly until the solution was completely absorbed into the sieves. Two further portions of ethanol (100 mL), were added and then soaked up by more molecular sieves. The molecular sieves were soaked in ethanol for 3 h, then overnight in ethanol. This was repeated twice, soaking overnight in methanol. Alcohol was removed *in vacuo*, yielding a pale yellow viscous liquid (24 g).

All four were approximately 90% tris(diethanolamino)cyclopropenium chloride, with 10% $[H_2N(C_2H_4OH)_2]Cl$. Molecular sieves were washed with excess water, and the process was repeated to remove $[H_2N(C_2H_4OH)_2]Cl$, which a yielded a pale yellow, extremely viscous liquid (7.0 g, 16%). ^{1}H NMR (D_2O, 300MHz): δ 3.81 (t, $^3J_{HH}$ = 5.3 Hz, 12H, NCH_2), 3.61 ppm (t, $^3J_{HH}$ = 5.3 Hz, 12H, NCH_2CH_2). ES^+ m/z 348.2158 (100%, M^+). ^{13}C NMR as for cation of $[C_3(N(C_2H_4OH)_2)_3]I$.

2.3 Synthesis of bis(diisopropylamino)dialkylaminocyclopropenium salts

2.3.1 Chlorobis(diisopropylamino)cyclopropenium chloride, $[C_3(N\mathit{i}Pr_2)_2Cl]Cl$[4,5]

Bis(diisopropylamino)cyclopropenone (4.69 g, 18.6 mmol) was added to an excess of freshly distilled $SOCl_2$ (10 mL, 137 mmol) at 0 °C, and stirred for 3 h. $SOCl_2$ was removed *in vacuo* to yield a solid orange product (5.29 g, 95 %). ^{1}H NMR (300 MHz, $CDCl_3$): 4.23 (spt, $^3J_{HH}$ = 6.15 Hz, $NCH(CH_3)_2$), 3.87 (spt, $^3J_{HH}$ = 6.15 Hz, $NCH(CH_3)_2$), 1.41 (m, $NCH(CH_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$): 132.25 (C_2), 93.11 (C_1), 58.13 ($NCH(CH_3)_2$), 48.33 ($NCH(CH_3)_2$), 22.60 ($NCH(CH_3)_2$), 20.96 ($NCH(CH_3)_2$).

2.3.2 Bis(diisopropylamino)dibutylaminocyclopropenium chloride, $[C_3(N^{\mathit{i}}Pr_2)_2NBu_2]Cl$

C_3Cl_5H (5.17 g, 24.1 mmol) was stirred at 0 °C in dry dichloromethane (75 mL). $HN^{\mathit{i}}Pr_2$ (11.9 g, 118 mmol) added dropwise over 1 h followed by stirring for 2 h at 0 °C and then overnight at ambient temperature. $HN^{\mathit{n}}Bu_2$ (12.3 g, 95.0 mmol) was added dropwise over 1 h, followed by stirring for 2 h at 0 °C, then overnight at ambient temperature, then heated to reflux for 4 h. The dichloromethane was removed *in vacuo* and dilute NaOH added. The aqueous solution was washed with diethyl ether (3 x 75 mL). The solution was neutralized with aqueous HCl and the product extracted with dichloromethane (3 x 125 mL). Drying *in vacuo* yielded a colourless solid (5.77 g, 60%). ^{1}H NMR (300 MHz, $CDCl_3$): 3.79 (spt, $^3J_{HH}$ = 13.8, 7.0 Hz, 4H, $NCH(CH_3)_2$), 3.36 (t, $^3J_{HH}$ = 7.9 Hz, 4H, NCH_2), 1.53 (m, 4H, NCH_2CH_2), 1.30 (d, $^3J_{HH}$ = 7.0 Hz, 24H, $NCH(CH_3)_2$), 1.23 (m, 4H, $NCH_2CH_2CH_2$), 0.89 (t, $^3J_{HH}$ = 7.90 Hz, 6H, CH_2CH_3). ^{13}C NMR (75 MHz, $CDCl_3$):

118.46 (C_1), 117.49 (C_2), 51.57 (N*C*H_2), 51.50 (N*C*H(CH_3)$_2$), 30.77 (NCH$_2$*C*H_2), 21.99 (NCH(*C*H_3)$_2$), 19.44 (N(CH_2)$_2$*C*H_2CH$_3$), 13.67 (N(CH_2)$_3$*C*H_3). ES^+ m/z 364.3690 (100%, M^+). Found: C, 67.83; H, 11.48; N, 10.50%. Calc. for $C_{23}H_{46}N_3Cl.0.40H_2O$: C, 67.83; H, 11.58; N, 10.32%.

2.3.3 Bis(diisopropylamino)dibutylaminocyclopropenium bis(trifluoromethanesulfonyl)amide, [C_3(N^{i}Pr$_2$)$_2$NBu$_2$]TFSA

[C_3(N^{i}Pr$_2$)$_2$NBu$_2$]Cl (0.302 g, 0.755 mmol) was stirred with LiTFSA (0.650 g, 2.27 mmol) in water (50 mL). The product was extracted with chloroform (50 mL). Additional LiTFSA (0.804 g, 2.81 mmol) in water (50 mL) was added. The chloroform was washed with water (3 x 50 mL) and dried *in vacuo* to yield a colourless solid (0.30 g, 62%). ^{1}H, ^{13}C NMR and MS^+ as for [C_3(N^{i}Pr$_2$)$_2$NBu$_2$]Cl. Found: C, 47.23; H, 7.26; N, 8.62%. Calc. for $C_{25}H_{46}N_4S_2O_4F_6$: C, 46.57; H, 7.19; N, 8.69%. Cl^- content: 2471 ppm.

2.3.4 Bis(diisopropylamino)dibutylaminocyclopropenium dicyanamide, [C_3(N^{i}Pr$_2$)$_2$NBu$_2$]DCA

[C_3(N^{i}Pr$_2$)$_2$NBu$_2$]Cl (0.300 g, 0.750 mmol) was stirred with NaDCA (0.350 g, 3.93 mmol) in water (50 mL). The product was extracted with chloroform (50 mL). Additional NaDCA (0.519 g, 5.83 mmol) in water (50 mL) was added . The chloroform was washed with water (3 x 50 mL) and dried *in vacuo* to yield a colourless solid (0.25 g, 78%). ^{1}H, ^{13}C NMR and MS^+ as for [C_3(N^{i}Pr$_2$)$_2$NBu$_2$]Cl. Found: C, 69.67; H, 10.76; N, 19.64%. Calc. for $C_{25}H_{46}N_4S_2O_4F_6$: C, 69.72; H, 10.77; N, 19.51%. Cl^- content: 1176 ppm.

2.3.5 bis(diisopropylamino)butylmethylaminocyclopropenium, [C_3(N*i*Pr$_2$)$_2$NBuMe]Cl

Chlorobis(diisopropylamino)cyclopropenium chloride (2.90 g, 9.4 mmol) was added to dichloromethane (20 mL). Excess HNBuMe (2.47 g, 28.3 mmol) was added and heated to reflux for 3 h. Dichloromethane was removed *in vacuo* and product dissolved in water (20 mL), washed with pet ether (20 mL) and extracted with a mixture of diethyl ether and dichloromethane (2 x 20 mL, 1:1 ratio). Dichloromethane and diethyl ether was removed *in vacuo* and yielded a brown solid (1.5 g, 49.6 %). ^{1}H NMR (300 MHz, $CDCl_3$): 3.86

(spt, $^3J_{HH}$ = 6.74 Hz, NC*H*$(CH_3)_2$), 3.48 (t, $^3J_{HH}$ = 7.91, NC*H*$_2$$CH_2CH_2CH_3$), 3.28 (s, NC*H*$_3$), 1.94 (m, NCH_2C*H*$_2$$CH_2CH_3$), 1.64 (m, NCH_2CH_2C*H*$_2$$CH_3$), 1.36 (d, $^3J_{HH}$ = 6.74 Hz, NCH(C*H*$_3$)$_2$), 0.94 (t, $NCH_2CH_2CH_2$C*H*$_3$).

2.4 Unsuccessful syntheses of less symmetric triaminocyclopropenium salts

2.4.1 Chlorobis(diethylamino)cyclopropenium, $[C_3(NEt_2)_2Cl]^+$ (0 °C, no base)

C_3Cl_5H (1.67 g, 7.8 mmol) stirred in dichloromethane (25 mL) at 0 °C. $HNEt_2$ (2.84 g, 38.8 mmol) added dropwise and stirred for 5 h. Stirred with 35% HBF_4 (25 mL), then separated organic layer and removed solvent by vacuum. Yielded pure $[C_3(NEt_2)_3]BF_4$ (1.71 g, 64.7 %). ^{1}H, ^{13}C NMR and MS^+ as for $[C_3(NEt_2)_3]Cl$.

2.4.2 Bis(diethylamino)dibutylaminocyclopropenium, $[C_3(NEt_2)_2NBu_2]^+$ (0 °C, no base)

C_3Cl_5H (5.00 g, 23.3 mmol) stirred in dichloromethane (100 mL) at 0 °C. $HNEt_2$ (8.51 g, 116.5 mmol) added dropwise and stirred overnight. HN^nBu_2 (13.69 g, 106.0 mmol) was added, followed by heating to reflux for 4 h. Dichloromethane was removed *in vacuo*, aqueous NaOH was added and the solution was washed with diethyl ether (3 x 50 mL). The solution was neutralized with HCl acid, extracted with dichloromethane (4 x 25 mL) and washed with water (2 x 25 mL). Dichloromethane was removed *in vacuo*, yielding a brown liquid (2.10 g). ^{1}H and ^{13}C NMR spectra showed a complex mixture of products. ES^+ *m/z*: 252 (100 %, $[C_3(NEt_2)_3]^+$), 308 (80 %, $[C_3(NEt_2)_2NBu_2]^+$), 364 (65 %, $[C_3(NBu_2)_2NEt_2]^+$), 420 (25 %, $[C_3(NBu_2)_3]^+$).

2.4.3 Bis(diethylamino)butylmethylaminocyclopropenium, $[C_3(NEt_2)_2NBuMe]^+$ (0 °C, NEt_3)

Dry triethylamine (distilled from KOH, 5 mL) was added dropwise to dichloromethane (45 mL) at 0 °C. C_3Cl_5H (1.67 g, 7.8 mmol) was added dropwise, followed by $HNEt_2$ (1.14 g, 15.5 mmol). After stirring at ambient temperature overnight, HN^nBuMe (0.68 g, 7.8 mmol) added and heated to reflux at for 5 h. Dichloromethane removed *in vacuo*,

dissolved in water (40 mL) and washed with pet ether (2 x 40 mL) to remove excess triethylamine, followed by extraction with dichloromethane. Dichloromethane was removed *in vacuo*. ^{1}H and ^{13}C NMR spectra showed a complex mixture of products. ES^{+} *m/z*: 252 (100%, $[C_3(NEt_2)_3]^{+}$), 266 (5%, $[C_3(NEt_2)_2NBuMe]^{+}$), 280 (5%, $[C_3(NBuMe)_2NEt_2]^{+}$), 294 (2%, $[C_3(NBuMe)_3]^{+}$).

2.4.4 Bis(diethylamino)butylmethylaminocyclopropenium, $[C_3(NEt_2)_2NBuMe]^{+}$ (-78 °C, NEt_3)

C_3Cl_5H (3.34 g, 15.6 mmol) stirred in dichloromethane (75 mL) at –78 °C. Added NEt_3 (25 mL) followed by $HNEt_2$ (2.28 g, 31.2 mmol) added dropwise and stirred for 2 h at –78 °C. Removed from cold bath and allowed to warm to ambient temperature over 1 h. Cooled to –78 °C again and added HNBuMe (1.36 g, 15.6 mmol). Stirred at ambient temperature for 60 h, followed by heating to reflux for 5 h. Dichloromethane was removed *in vacuo*, added acetone (50 mL) and filtered off ammonium salt precipitate. Acetone was removed *in vacuo*, followed by addition of dichloromethane (50 mL) and washed with water (3 x 50 mL). Removal of dichloromethane *in vacuo* yielded a brown liquid (1.35 g, ~33%). ^{1}H and ^{13}C NMR spectra showed a complex mixture of products.

2.4.5 Bis(diethylamino)butylmethylaminocyclopropenium, $[C_3(NEt_2)_2NBuMe]^{+}$ (0 °C, $KO^{t}Bu$)

C_3Cl_5H (1.67 g, 7.8 mmol) was stirred in dichloromethane (20 mL) at 0 °C. $HNEt_2$ (1.14 g, 15.5 mmol) was added, followed immediately by $K^{t}BuO$ (3.49 g, 31.6 mmol). After stirring at ambient temperature overnight, $HN^{n}BuMe$ (0.68 g, 7.8 mmol) was added. Dichloromethane was removed *in vacuo*, dissolved in water and washed with pet ether (4 x 20 mL). Extracted with dichloromethane (40 mL), and removed solvent *in vacuo*, yielding a brown liquid. ^{1}H and ^{13}C NMR spectra showed a complex mixture of products. ES^{+} *m/z*: 252 (100%, $[C_3(NEt_2)_3]^{+}$), 266 (25%, $[C_3(NEt_2)_2NBuMe]^{+}$), 280 (15%, $[C_3(NBuMe)_2NEt_2]^{+}$), 294 (40%, $[C_3(NBuMe)_3]^{+}$).

2.4.6 Bis(diethylamino)dibutylaminocyclopropenium, $[C_3(NEt_2)_2NBu_2]^+$ (-78 °C, KO^tBu)

C_3Cl_5H (1.67 g, 7.8 mmol) stirred in dichloromethane (25 mL) at –78 °C. $HNEt_2$ (1.14 g, 15.5 mmol) added and stirred for 1 h at –78 °C. Added excess KO^tBu (4 g, 35.7 mmol), continued stirring for 2 h at –78 °C. Added excess HN^nBu_2 (1.53 g, 11.9 mmol). After stirring overnight at ambient temperature, solution was neutralized with HCl acid and dichloromethane was removed *in vacuo*. Water (40 mL) added, and washed with pet ether (40 mL), then extracted product with dichloromethane (40 mL). Removal of dichloromethane *in vacuo* yielded a light brown liquid. ^1H and ^{13}C NMR spectra showed a complex mixture of products. ES^+ *m/z*: 252 (100 %, $[C_3(NEt_2)_3]^+$), 308 (5 %, $[C_3(NEt_2)_2NBu_2]^+$), 364 (5 %, $[C_3(NBu_2)_2NEt_2]^+$), 420 (5 %, $[C_3(NBu_2)_3]^+$).

2.4.7 Bis(diethylamino)butylmethylaminocyclopropenium, $[C_3(NEt_2)_2NBuMe]^+$ (0 °C, NaH)

C_3Cl_5H (3.34 g, 15.6 mmol) stirred in dichloromethane (25 mL) at 0 °C. $HNEt_2$ (2.27 g, 31.1 mmol) added dropwise, followed by NaH (1.45 g, 60.6 mmol). After heating to reflux at 60 °C for 4 h, cooled to 0 °C and HN^nBuMe (1.36 g, 15.6 mmol) was added, followed by another 1.3 equivalents of NaH (0.508 g, 21.2 mmol). Water (40 mL) was added and acidified with HCl acid, followed by removal of dichloromethane *in vacuo*. The solution was washed with pet ether (2 x 20 mL). Water was removed *in vacuo* and acetone (75 mL) was added to precipitate NaCl, which was filtered off. Removal of acetone *in vacuo* yielded a brown liquid. ^1H and ^{13}C NMR spectra showed a complex mixture of products.

2.4.8 Bis(diethylamino)butylmethylaminocyclopropenium, $[C_3(NEt_2)_2NBu_2]^+$ (-78 °C, DBU)

C_3Cl_5H (3.34 g, 15.6 mmol) was stirred in dichloromethane (50 mL) at 0 °C. 1,8-diazabicyclo[5.4.0]undec-7-ene (11.8 g, 77.8 mmol) was added dropwise to the solution, then cooled to –78 °C, followed by addition of $HNEt_2$ (2.29 g, 31.3 mmol) dropwise and stirred for 2 h at –78 °C. The solution was stirred at ambient temperature overnight, then added HNBuMe (1.35 g, 15.6 mmol) and continued stirring for 2 h, then heated to reflux

for 3.5 h. Added additional dichloromethane (50 mL) and unintentionally extracted with water (5 x 100 mL). Extracted with dichloromethane (3 x 100 mL). Removal of dichloromethane *in vacuo* yielded a brown liquid. ^{1}H and ^{13}C NMR spectra showed a complex mixture of products.

2.5 Alkylation of bis(dialkylamino)cyclopropenone

2.5.1 Alkylation using iodoalkane

Cyclopropenone $(Et_2N)_2C_3O$ was stirred with the iodoalkane and heated to reflux. After the desired length of time, the reaction was allowed to cool to ambient temperature and washed with pet ether to remove the iodo alkane. The crude product was a brown liquid, which was a mixture of the triaminocyclopropenium salt, $(Et_2N)_2C_3O$ and ammonium salts. ^{1}H NMR was used to find the ratio of triaminocyclopropenium salt to $(Et_2N)_2C_3O$. The results are covered in the table below.

Table 2-1 – Synthesis of triaminocyclopropenium salts via $(Et_2N)_2C_3O$ using iodoalkanes

Alkylating agent	Equivalents	Time / h	Solvent	Ratio of product to $(Et_2N)_2C_3O$)
EtI	5	2	–	2.21
EtI	5	20	–	2.40
EtI	20	2	–	0.57
EtI	20	20	–	4.00
MeI	10	20	–	0.18
^{i}PrI	5	16	$C_2H_4Cl_2$	4.89

2.5.2 Alkylation with Me_2SO_4

Cyclopropenone $(Et_2N)_2C_3O$ (0.10 g, 0.51 mmol) and dimethylsulfate (0.13 g, 1.02 mmol) were mixed in a 5 mm NMR tube. ^{13}C NMR (75 MHz): δ 121.22 (C_2), 119.88 (CO), 63.75 (OCH_3), 59.88 ($(OCH_3)_2SO_2$), 53.12 ($[(OCH_3)SO_3]^-$), 47.42 (NCH_2CH_3), 46.48 (small, NCH_2CH_3, $(Et_2N)_2C_3O$), 14.11 (small, NCH_2CH_3, $(Et_2N)_2C_3O$), 13.64 (NCH_2CH_3). Immediately following the ^{13}C NMR, $HN^{n}BuMe$ (0.26 g, 3.0 mmol) was added, and another ^{13}C NMR ran after 5 min. ^{13}C NMR (75 MHz): 120.15 (C_1), 118.97 (C_2), 16-68ppm contains multiple peaks, $[C_3(NEt_2)_2NBuMe]^+$, Me_2SO_4, $[MeSO_4]^-$, ammonium salts.

2.5.3 Attempted alkylation with Me_2CO_3

Cyclopropenone $(Et_2N)_2C_3O$ (5.00 g, 25.5 mmol) was added to dimethylcarbonate (46.1 g, 511 mmol) and heated to reflux (90 °C) for 18 h. The reaction mixture was cooled to 0 °C and HNBuMe (11.6 g, 133 mmol) was added. After 1 h, water (150 mL) was added and the solution was washed with pet ether (2 x 50 mL). The product was extracted with chloroform (2 x 100 mL) and washed with water (2 x 75 mL) to remove ammonium salts. Removal of solvent *in vacuo* yielded an orange liquid. ^{1}H NMR showed $(Et_2N)_2C_3O$.

2.6 Unsuccessful reactions of bis(dialkylamino)cyclopropenone

2.6.1 Bis(diethylamino)cyclopropenone with dialkylammonium salt

Cyclopropenone $(Et_2N)_2C_3O$ (0.25 g, 1.28 mmol) was dissolved in dichloromethane (50 mL), followed by addition of $[H_2NBuMe]BF_4$ (0.22 g, 1.91 mmol) and the mixture was heated to reflux for 18 h. Dichloromethane was removed *in vacuo*, chloroform (25 mL) was added and washed with water (2 x 25 mL). Removal of solvent *in vacuo* yielded an orange liquid. ^{1}H NMR showed this to be $(Et_2N)_2C_3O$.

2.6.2 Bis(diethylamino)cyclopropenone with dialkylamine

Cyclopropenone $(Et_2N)_2C_3O$ (0.440 g, 2.24 mmol) was added to HNBuMe (3.68 g, 42.2 mmol) and the mixture was heated to reflux for 18 h. Water (50 mL) was added and neutralized with aqueous HCl. The crude product was extracted with chloroform (25 mL) and the solution was washed with water (25 mL). Removal of solvent *in vacuo* yielded an orange liquid. ^{1}H NMR showed this to be $(Et_2N)_2C_3O$.

2.6.3 Bis(diethylamino)cyclopropenone with potassium dialkylamide

KO^tBu (0.148 g, 1.32 mmol) was added to HNBuMe (2.21 g, 25.3 mmol). After 3h, cyclopropenone $(Et_2N)_2C_3O$ (0.270 g, 1.38 mmol) was added to the mixture and it was stirred at 60 °C for 3 h. Water (25 mL) was added and the solution was neutralized with aqueous HCl. The crude product was extracted with chloroform (25 mL) and the solution washed with water (25 mL). Removal of solvent *in vacuo* yielded an orange liquid. ^{1}H NMR showed this to be $(Et_2N)_2C_3O$.

2.6.4 Bis(diethylamino)cyclopropenone with sodium dialkylamide

NaH (0.029 g, 1.21 mmol, dispersion in mineral oil) was added to HNBuMe amine (2.21 g, 25.3 mmol). After 3 h, cyclopropenone $(Et_2N)_2C_3O$ (0.246 g, 1.26 mmol) was added to the mixture and it was stirred for 18 h. Water (25 mL) was added and the solution neutralized with aqueous HCl. The crude product was extracted with chloroform (25 mL) and the solution washed with water (25 mL). Removal of solvent *in vacuo* yielded an orange liquid. ^{1}H NMR showed this to be $(Et_2N)_2C_3O$.

2.7 Ionic liquid fluorides

2.7.1 Tris(dipropylamino)cyclopropenium fluoride diethanol, $[C_3(NPr_2)_3]F.1.9EtOH$

$[C_3(NPr_2)_3]Cl$ (10.6 g, 28.5 mmol) was stirred in water (450 mL), in a blacked-out flask, to which Ag_2O (6.7 g, 28.9 mmol) was added and continued stirring for 3 h. AgCl precipitated, and was removed by filtering through Celite, before the solution was neutralized to pH 7.1 with aqueous HF. The solution was reduced in volume to 50 mL *in vacuo*, with drying being completed with ethanol azeotrope drying (3 x 500 mL), which yielded the product as an orange liquid (12.4 g, 97%). ^{1}H NMR (300 MHz, $CDCl_3$): 3.68 (q, $^3J_{HH}$ = 7.03 Hz, 3.81H, CH_3CH_2OH), 3.27 (t, $^3J_{HH}$ = 7.91 Hz, 12H, $NCH_2CH_2CH_3$), 1.67 (m, 12H, $NCH_2CH_2CH_3$), 1.21 (t, $^3J_{HH}$ = 7.03 Hz, 5.00H, CH_3CH_2OH), 0.94 (t, $^3J_{HH}$ = 7.33 Hz, 18H, $NCH_2CH_2CH_3$). ^{19}F NMR (282 MHz, D_2O, C_6H_5F): 122.03 (s). Found: C, 61.95; H, 12.48; N, 8.77%. Calc. for $C_{21}H_{42}N_3F.1.9EtOH.2.09H_2O$: C, 61.95; H, 12.07; N, 8.74%. H_2O content: 2200 ppm. F^- content: 44300 ppm, calculated: 42900 ppm.

2.7.2 Tris(dipropylamino)cyclopropenium fluoride ethanol, $[C_3(NPr_2)_3]F.1.1EtOH$

To remove one EtOH solvated molecule from $[C_3(NPr_2)_3]F.2EtOH$ (2.5 g, 5.6 mmol), a benzene azeotrope was used. Benzene (20 mL) added and the solvent removed *in vacuo*, followed by a further two additions and removals of solvent *in vacuo* of benzene (10 mL). This yielded a brown liquid (2.02 g), which included 17% bis(dipropylamine)cyclopropenone and $HNPr_2$. ^{1}H NMR (300 MHz, $CDCl_3$): 3.67 (q, $^3J_{HH}$ = 7.03 Hz, 2.25H, CH_3CH_2OH), 3.26 (t, $^3J_{HH}$ = 7.91 Hz, 12H, $NCH_2CH_2CH_3$), 3.15

(t, $^3J_{HH}$ = 7.33 Hz, 1.61H, bis(dipropylamino)cyclopropenone), 2.70 (t, $^3J_{HH}$ = 7.91 Hz, 1.36H, $HNPr_2$), 1.66 (m, 12H, $NCH_2CH_2CH_3$), 1.44 (m, 2.98 H, bis(dipropylamino)cyclopropenone and $HNPr_2$), 1.20 (t, $^3J_{HH}$ = 7.03 Hz, 3.41H, CH_3CH_2OH), 0.93 (t, $^3J_{HH}$ = 7.33 Hz, 18H, $NCH_2CH_2CH_3$), 0.80 (m, 5.33 H, bis(dipropylamino)cyclopropenone and HN^nPr_2). ^{13}C NMR and MS^+ as for cation of $[C_3(NPr_2)_3]Cl$. Found: C, 67.07; H, 12.16; N, 9.39%. Calc. for $C_{21}H_{42}N_3F.1.1EtOH.0.92H_2O$, 17% P4O: C, 67.09; H, 12.07; N, 9.12%.

2.7.3 Bis(diethylamino)diethanolaminocyclopropenium fluoride diethanol, $[C_3(NEt_2)_2N(C_2H_4OH)_2]F.1.9EtOH$

$[C_3(NEt_2)_2N(C_2H_4OH)_2]I$ (3.50 g, 8.52 mmol) was stirred in water (250 mL), in a blacked-out flask, to which Ag_2O (3.0 g, 13 mmol) was added and continued stirring for 3 h. AgI precipitated, and was removed by filtering through Celite, before the solution was neutralized to pH 7.5 with aqueous HF. The solution was reduced in volume to 20 mL *in vacuo*, with drying being completed with ethanol azeotrope drying (3 x 200 mL), which yielded the product as a viscous yellow liquid (2.5 g, 96%).^1H NMR and ^{13}C NMR as for $[C_3(NEt_2)_2N(C_2H_4OH)_2]I$. ^{19}F NMR (282 MHz, D_2O, C_6H_5F reference): 121.94 (s).

2.7.4 Tris(diethanolamino)cyclopropenium fluoride, $[C_3(N(C_2H_4OH)_2)_3]F$

$[C_3(C_2H_4OH)_3]Cl$ (7.0 g, 19 mmol) was dissolved into water (250 mL), and Ag_2O (7.0 g, 30 mmol) was added and stirred for 3 h, in a blacked out flask. Water was partially (200 mL) removed *in vacuo*. AgCl formed, and was removed by filtering through celite, before the solution was neutralized to pH 7.5 with aqueous HF. Complete drying was achieved with additions (3 x 150 mL, 3 x 50 mL) of ethanol and isopropanol and removal of the solvent *in vacuo*. This was followed by extended drying under a high vaccum, with stirring and mild heat (40 °C), which yielded a colourless solid (5.63 g, 84%). ^1H NMR as for $[C_3(N(C_2H_4OH)_2)_3]Cl$. ^{19}F NMR (282 MHz, D_2O, C_6H_5F): 122.05 (s). ^{13}C NMR (75 MHz, D_2O, acetonitrile reference): 118.18 (C_3), 59.38 (NCH_2CH_2OH), 54.29 (NCH_2CH_2OH).

2.7.5 Tris(diethanolamino)cyclopropenium Fluoride, $[C_3(N(C_2H_4OH)_2)_3]F$

$[C_3(C_2H_4OH)_3]Cl$ (3.0 g, 7.8 mmol) was dissolved into water (200 mL), and AgF (1.30 g, 10.2 mmol) added and stirred. AgCl precipitated, and was removed by filtering through Celite. Excess AgF was removed by removal of solvent *in vacuo*, followed by the addition of alcohol solvent (50 mL, 5 x ethanol then 5 x isopropanol), after each addition solution was filtered through Celite and solvent removed *in vacuo*. This yielded a light yellow, extremely viscous liquid (2.3 g, 80%). Found: C, 48.82; H, 8.09; N, 11.06%. Calc. for $C_{15}H_{30}N_3O_6F$: C, 49.04; H, 8.23; N, 11.44%. Cl^- content: 1600 ppm.

2.7.6 Tris(dipropylamino)cyclopropenium fluoride, $[C_3(NPr_2)_3]F$ (sodium isopropoxide method)

Sodium (0.3 g, 13 mmol) was added to isopropanol (50 mL) and stirred overnight to dissolve it. [P6]Cl (2.53 g, 6.82 mmol) was dissolved into isopropanol (25 mL) and mixed with the sodium isopropoxide solution. A precipitate of NaCl formed and this was filtered off. The isopropanol solution was added into water (600 mL) and neutralized with aqueous HF acid. Cl^- content of solution: 31 ppm.

2.7.7 1-Ethyl-3-methylimidazolium fluoride diethanol, [EMIM]F.1.8EtOH

[EMIM]Cl (33.0 g, 225 mmol) was dissolved into ethanol (500 mL). KF (30 g, 520 mmol) was partially dissolved into ethanol (250 mL) and the solutions were stirred together for 1 h, followed by filtering the solid precipitate off. This was repeated twice more with KF (35 and 25 g). The solvent was reduced in volume *in vacuo*, and acetonitrile (250 mL) was added and the solution cooled. A precipitate formed, and was filtered off. Ethanol was added to the filtrate, and excess solvent removed *in vacuo*. Cl^- content: 3120 ppm. The [EMIM]F ethanol solvate (52 g) was dissolved in water (200 mL). AgF (550 mg, 4.34 mmol) was dissolved in water (100 mL) and the solutions mixed together. AgCl precipitated out of solution and was filtered off. The solvent volume was reduced *in vacuo*, and drying completed using ethanol azeotropes. The product was a pale yellow liquid (41.9 g, 87%), with 1.83 ethanol solvate molecules per fluoride. ^1H NMR (400 MHz, D_2O): 7.40 (d, $^3J_{HH}$ = 1.96 Hz, CH), 7.33 (d, $^3J_{HH}$ = 1.96 Hz, CH), 4.14 (q,

$^{3}J_{HH}$ = 7.66 Hz, C*H*$_2$CH$_3$), 3.80 (s, C*H*$_3$), 3.56 (q, $^{3}J_{HH}$ = 7.34 Hz, CH$_3$C*H*$_2$OH), 1.41 (t, $^{3}J_{HH}$ = 7.34 Hz, CH$_2$C*H*$_3$), 1.09 (t, $^{3}J_{HH}$ = 7.34 Hz, C*H*$_3$CH$_2$OH). ^{19}F NMR (377 MHz, D$_2$O, CFCl$_3$): -121.22 (s). Cl^- content: 69 ppm. K^+ content: <100 ppm. Ag^+ content: 821 ppm.

2.7.8 1-Ethyl-3-methylimidazolium fluoride acetic acid, [EMIM]F.1.01AcOH

Acetic acid (1.77 g, 29.4 mmol) was added to [EMIM]F.1.8EtOH (6.31 g, 29.4 mmol). The mixture was dried with isopropanol (2 x 50 mL) and ethanol (50 mL) azeotropes. Additional acetic acid (0.111 g, 1.85 mmol) was then added. The product was a pale yellow liquid (5.04 g, 90%). ^{1}H NMR (400 MHz, D$_2$O): 8.63 (s, C*H*), 7.41 (C*H*), 7.35 (C*H*), 4.15 (q, $^{3}J_{HH}$ = 7.34 Hz, C*H*$_2$CH$_3$), 3.82 (s, C*H*$_3$), 1.94 (s, C*H*$_3$CO$_2$HF), 1.43 (t, $^{3}J_{HH}$ = 7.34 Hz, CH$_2$C*H*$_3$). ^{19}F NMR (377 MHz, D$_2$O): -128.87 (s, CH$_3$CO$_2$H*F*), –142.77 (m, *F*$_2$H$^-$), 27.1:1 ratio. H$_2$O content: 1330 ppm.

2.7.9 1-Ethyl-3-methylimidazolium fluoride acetic acid, [EMIM]F.1.57AcOH

Acetic acid (3.00 g, 50.0 mmol) was added to [EMIM]F.1.8EtOH (6.25 g, 29.2 mmol). The mixture was dried with an ethanol (50 mL) azeotrope, followed by drying for 5 h *in vacuo*. The product was a pale yellow liquid (6.50 g, 99%). ^{1}H NMR (400 MHz, D$_2$O): 8.63 (s, C*H*), 7.41 (C*H*), 7.35 (C*H*), 4.15 (q, $^{3}J_{HH}$ = 7.34 Hz, C*H*$_2$CH$_3$), 3.82 (s, C*H*$_3$), 1.95 (s, C*H*$_3$CO$_2$HF), 1.42 (t, $^{3}J_{HH}$ = 7.58 Hz, CH$_2$C*H*$_3$). ^{19}F NMR (377 MHz, D$_2$O): –128.88 (s, CH$_3$CO$_2$H*F*), –142.49 (m, *F*$_2$H$^-$), 24.0:1 ratio. H$_2$O content: 1240 ppm.

2.7.10 1-Ethyl-3-methylimidazolium fluoride acetic acid, [EMIM]F.2.08AcOH

Acetic acid (3.58 g, 59.6 mmol) was added to [EMIM]F.1.8EtOH (6.39 g, 29.8 mmol). The mixture was dried with ethanol (3 x 50 mL) azeotropes. Additional acetic acid (0.535 g, 8.91 mmol) was then added. The product was a pale yellow liquid (7.28 g, 96%). ^{1}H NMR (400 MHz, D$_2$O): 8.62 (s, C*H*), 7.40 (C*H*), 7.33 (C*H*), 4.14 (q, $^{3}J_{HH}$ = 7.34 Hz, C*H*$_2$CH$_3$), 3.80 (s, C*H*$_3$), 1.95 (s, C*H*$_3$CO$_2$HF), 1.41 (t, $^{3}J_{HH}$ = 7.34 Hz, CH$_2$C*H*$_3$). ^{19}F NMR (377 MHz, D$_2$O): –128.81 (s, CH$_3$CO$_2$H*F*), –142.48 (m, *F*$_2$H$^-$), 28.4:1 ratio. H$_2$O content: 1030 ppm.

2.7.11 1-Ethyl-3-methylimidazolium fluoride acetic acid, [EMIM]F.2.44AcOH

Acetic acid (4.09 g, 68.1 mmol) was added to [EMIM]F.1.8EtOH (5.83 g, 27.2 mmol). The mixture was dried with ethanol (2 x 50 mL) azeotropes. Additional acetic acid (0.495 g, 8.24 mmol) was then added. The product was a pale yellow liquid (7.48 g, 99%). ^{1}H NMR (400 MHz, D_2O): 8.60 (s, C*H*), 7.39 (C*H*), 7.32 (C*H*), 4.13 (q, $^{3}J_{HH}$ = 7.34 Hz, C*H*$_2$CH$_3$), 3.79 (s, C*H*$_3$), 1.95 (s, C*H*$_3$CO$_2$HF), 1.39 (t, $^{3}J_{HH}$ = 7.34 Hz, CH$_2$C*H*$_3$). ^{19}F NMR (377 MHz, D_2O): –128.75 (s, CH$_3$CO$_2$H*F*), –142.46 (m, *F*$_2$H$^-$), 16.1:1 ratio. H_2O content: 1580 ppm.

2.7.12 1-Ethyl-3-methylimidazolium fluoride acetic acid, [EMIM]F.3.22AcOH

Acetic acid (3.76 g, 62.6 mmol) was added to [EMIM]F.1.8EtOH (4.47 g, 20.8 mmol). The mixture was dried with ethanol (2 x 50 mL) azeotropes. Additional acetic acid (0.825 g, 13.7 mmol) was then added. The product was a pale yellow liquid (5.20 g, 77%). ^{1}H NMR (400 MHz, D_2O): 8.62 (s, C*H*), 7.40 (C*H*), 7.34 (C*H*), 4.14 (q, $^{3}J_{HH}$ = 7.34 Hz, C*H*$_2$CH$_3$), 3.81 (s, C*H*$_3$), 1.98 (s, C*H*$_3$CO$_2$HF), 1.42 (t, $^{3}J_{HH}$ = 7.34 Hz, CH$_2$C*H*$_3$). ^{19}F NMR (377 MHz, D_2O): –128.80 (s, CH$_3$CO$_2$H*F*), –142.57 (m, *F*$_2$H$^-$), 20.4:1 ratio. H_2O content: 900 ppm.

2.7.13 (2-hydroxyethyl)trimethylammonium fluoride hydrate, choline fluoride hydrate

Choline chloride (10.2 g, 73.2 mmol) was dissolved into water (200 mL) in a blacked out flask. Ag_2O (12.7 g, 54.8 mmol) was added and the solution stirred for 4 h. AgCl precipitated, and was removed by filtering through Celite, before the solution was neutralized to pH 7.5 with aqueous HF. Water was removed by drying *in vacuo* at 40 °C for 72 h, yielding a while solid (9.89 g, 91%). Found: C, 40.34; H, 11.24; N, 9.03%. Calc. for $C_5H_{14}NOF.1.43H_2O$: C, 40.34; H, 11.41; N, 9.41%.

2.8 References

(1) Tobey, S. W.; West, R. *J. Am. Chem. Soc.* **1966**, 88, 2478-2481.

(2) Wilcox, C.; Breslow, R. *Tetrahedron* **1980**, 21, 3241-3242.

(3) Clark, G. R.; Surman, P. W. J.; Taylor, M. J. *J. Chem. Soc., Faraday Trans.* **1995**, 91, 1523-1528.

(4) Yoshida, Z.; Tawara, Y. *J. Am. Chem. Soc.* **1971**, 93, 2573-2574.

(5) Taylor, M. J.; Surman, P. W. J.; Clark, G. R. *J. Chem. Soc., Chem. Commun.* **1994**, 2517-2518.

Chapter 3

3 Results

This section summarizes the results of the properties measured: thermal, electrochemical and chemical stabilities, thermal behaviour, viscosity, conductivity, density and solubility or miscibility. For the samples where only solubility was measured, S stands for soluble, P for partial miscibility and N for insoluble. For the miscibility measurements, N stands for immiscible, M for miscible and the volume ratio of solvent:ionic liquid shows below what ratio it was miscible and above what ratio it was immiscible. For the chemical stability tests, Y stands for stable with no change in the ^{1}H-NMR, and N for degradation seen in the ^{1}H-NMR.

3.1 *D*$_{3h}$ cations

3.1.1 Tris(dimethylamino)cyclopropenium chloride, $[C_3(NMe_2)_3]Cl$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–31	–	–	–	–	179	221

3.1.2 Tris(dimethylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NMe_2)_3]TFSA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–	45	2.6	105	8.3	309	339
	65	1.9				
	83	2.2				

Solubility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	N	S	S	N	P	N

3.1.3 Tris(diethylamino)cyclopropenium chloride, $[C_3(NEt_2)_3]Cl$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–	–	–	92	16	273	306

Solubility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	S	S	S	N	N	N	N

Chemical Stability	HCl	KOH	NH_3	$NaBH_4$	$NaIO_4$	EtMgI
RT	Y	N	Y	Y	Y	Y
60 °C	Y	N	Y	Y	Y	Y

3.1.4 Tris(diethylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_3]TFSA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–86	–34 1	– 9.4	19	19	349	393

T / °C	20	30	40	50	60	70	80	90
η / mPa s	94.7	60.5	40.0	27.5	19.6	15.0	11.5	9.0
σ / mS cm^{-1}	1.39	1.98	2.76	3.68	4.75	5.97	7.35	8.86
ρ / g mL^{-1}	1.277	1.269	1.260	1.251	1.243	1.234	1.226	1.217

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	M	M	M	N	<1:1 M >2:1 N	N

Chemical Stability	HCl	KOH	NH_3	$NaBH_4$	$NaIO_4$	EtMgI
RT	Y	Y	Y	Y	Y	Y
60 °C	Y	N	Y	Y	Y	Y

3.1.5 Tris(diethylamino)cyclopropenium dicyanamide, $[C_3(NEt_2)_3]DCA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–	–	–	10	3.5	291	330

T / °C	20	30	40	50	60	70	80	90
η / mPa s	64.2	41.9	28.3	19.9	14.6	11.4	8.9	7.1
σ / mS cm^{-1}	4.69	6.80	9.20	11.97	15.14	18.63	22.40	26.33
ρ / g mL^{-1}	1.010	1.004	0.998	0.992	0.985	0.979	0.973	0.967

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	<0.7:1 M >0.8:1 N	M	M	M	<1:1 M >2:1 N	<1:1 M >2:1 N	N

Chemical Stability	HCl	KOH	NH_3	$NaBH_4$	$NaIO_4$	EtMgI
RT	Y	N	Y	Y	Y	Y
60 °C	Y	N	Y	Y	Y	Y

3.1.6 Tris(diethylamino)cyclopropenium tetrafluoroborate, $[C_3(NEt_2)_3]BF_4$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–	–	–	24	20	344	372

T / °C	20	30	40	50	60	70	80	90
η / mPa s [a]	206	115	69.3	43.7	29.4	21.0	15.5	11.8
ρ / g mL^{-1}	1.079	1.072	1.066	1.059	1.052	1.045	1.038	1.032

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	M	M	M	N	<1:1 M >2:1 N	N

[a] Carried out by Patrick Dronk, under supervision

3.1.7 Tris(diethylamino)cyclopropenium nitrate, $[C_3(NEt_2)_3]NO_3$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–66	–	–	31	5.0	230	265

T / °C	20	30	40	50	60	70	80	90
η / mPa s	313	169	98.5	61.3	41	28.8	20.6	–
ρ / g mL^{-1}	1.066	1.060	1.054	1.048	1.042	1.036	1.030	1.024

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	M	M	M	M	N	<0.8:1 M >1.1 N	N

3.1.8 Tris(diethylamino)cyclopropenium thiocyanate, $[C_3(NEt_2)_3]SCN$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–77	–	–	–3	13.1	283	311

T / °C	20	30	40	50	60	70	80	90
η / mPa s	134	79.1	49.7	33.5	23.5	17.2	12.9	10.0
ρ / g mL^{-1}	1.015	1.008	1.003	0.997	0.991	0.985	0.980	0.974

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	M	M	M	M	N	<1:1 M >2:1 N	N

3.1.9 Tris(diethylamino)cyclopropenium perchlorate, $[C_3(NEt_2)_3]ClO_4$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–65	–	–	39	23	241	274

T / °C	20	30	40	50	60	70	80	90
η / mPa s	–	–	136	81.7	52.5	35.8	25.3	18.5
σ / mS cm^{-1}	–	–	2.20	3.43	5.07	7.12	9.61	–
ρ / g mL^{-1}	–	–	1.114	1.108	1.101	1.095	1.088	1.082

Solubility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	P	S	S	S	N	P	N

3.1.10 Tris(dipropylamino)cyclopropenium chloride, $[C_3(NPr_2)_3]Cl$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–30	65	9.3	75	15	278	310

Solubility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	S	S	S	N	N	N	N

3.1.11 Tris(dipropylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NPr_2)_3]TFSA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–71	–2	1.9	30	20	364	413

T / °C	20	30	40	50	60	70	80	90
η / mPa s	220	127	78.3	50.1	32.3	22.6	16.6	12.6
σ / mS cm^{-1}	0.50	0.86	1.32	1.90	2.63	3.49	4.50	5.64
ρ / g mL^{-1}	1.196	1.188	1.179	1.171	1.163	1.155	1.147	1.139

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	M	M	M	<2:1 M >3:1 N	<1:1 M >2:1 N	N

3.1.12 Tris(dipropylamino)cyclopropenium dicyanamide, $[C_3(NPr_2)_3]DCA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–	–	–	49	26	295	317

T / °C	20	30	40	50	60	70	80	90
η / mPa s	–	–	–	–	14.6	10.2	7.5	5.7
σ / mS cm^{-1}	–	–	–	–	5.87	8.02	10.48	13.25
ρ / g mL^{-1}	–	–	–	–	0.951	0.945	0.939	0.933

Solubility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	P	S	S	S	N	P	N

3.1.13 Tris(dipropylamino)cyclopropenium tetrafluoroborate, $[C_3(NPr_2)_3]BF_4$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–	–	–	77	21	287	397

Solubility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	N	S	N	N	N	N

3.1.14 Tris(dipropylamino)cyclopropenium nitrate, $[C_3(NPr_2)_3]NO_3$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–55	–	–	–	–	286	301

T / °C	20	30	40	50	60	70	80	90
η / mPa s [a]	–	–	490	252	141	86.2	55.0	36.6
σ / mS cm^{-1}	0.07	0.18	0.37	0.68	1.06	1.35	1.94	2.66
ρ / g mL^{-1}	1.014	–	1.002	0.995	0.989	0.983	0.977	0.971

Solubility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	S	S	S	S	P	P	N

3.1.15 Tris(dibutylamino)cyclopropenium chloride, $[C_3(NBu_2)_3]Cl$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–40	–	–	41	–	264	303

T / °C	20	30	40	50	60	70	80	90
η / mPa s	–	–	–	1446	674	347	193	120
σ / mS cm^{-1}	–	–	–	0.08	0.16	0.31	0.53	0.86
ρ / g mL^{-1}	–	–	–	0.921	0.915	0.909	0.903	0.898

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	M	M	M	M	P	M	N

3.1.16 Tris(dibutylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NBu_2)_3]TFSA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–74	–	–	3	19	351	403

T / °C	20	30	40	50	60	70	80	90
η / mPa s	230	134	83.6	55.2	38.3	26.9	19.2	13.9
σ / mS cm^{-1}	0.43	0.69	1.06	1.54	2.14	2.92	3.82	4.87
ρ / g mL^{-1}	1.134	1.127	1.119	1.111	1.103	1.095	1.088	1.080

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	M	M	M	M	M	<0.5:1 M >0.6:1 N

3.1.17 Tris(dibutylamino)cyclopropenium dicyanamide, $[C_3(NBu_2)_3]DCA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–62	–	–	14	8.8	293	337

T / °C	20	30	40	50	60	70	80	90
η / mPa s	293	160	95.0	60.6	41.0	29.0	21.5	16.4
σ / mS cm^{-1}	–	1.16	1.89	2.89	4.16	5.73	7.58	9.68
ρ / g mL^{-1}	0.944	0.938	0.932	0.926	0.920	0.914	0.908	0.902

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	M	M	M	<1:1 M >2:1 N	M	<0.7:1 M >0.8:1 N

3.1.18 Tris(dibutylamino)cyclopropenium tetrafluoroborate, $[C_3(NBu_2)_3]BF_4$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–53	–	–	29	19	330	388

T / °C	20	30	40	50	60	70	80	90
η / mPa s [a]	–	546	276	153	89.9	56.8	37.5	26.4
σ / mS cm^{-1}	0.08	0.17	0.32	0.53	0.84	1.26	1.80	2.45
ρ / g mL^{-1}	0.993	0.986	0.980	0.973	0.967	0.960	0.954	0.947

Solubility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	S	S	S	P	S	P

3.1.19 Tris(dibutylamino)cyclopropenium nitrate, $[C_3(NBu_2)_3]NO_3$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–62	–	–	–	–	220	234

T / °C	20	30	40	50	60	70	80	90
η / mPa s	–	–	500	264	152	90.3	56.8	38.5
σ / mS cm^{-1}	0.07	0.16	0.32	0.59	0.97	1.57	2.34	–
ρ / g mL^{-1}	0.973	0.967	0.960	0.954	0.948	0.942	0.936	0.930

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	<0.1:1 M >0.2:1 N	M	M	M	<2:1 M >3:1 N	M	<0.4:1 M >0.5:1 N

3.1.20 Tris(dibutylamino)cyclopropenium triflate, $[C_3(NBu_2)_3]OTf$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–58	–	–	42	26	346	390

T / °C	20	30	40	50	60	70	80	90
η / mPa s	–	–	–	39.2	24.9	16.7	11.6	7.3
σ / mS cm^{-1}	–	–	–	0.87	1.34	1.96	2.75	3.71
ρ / g mL^{-1}	–	–	–	1.023	1.016	1.009	1.002	0.995

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	M	M	M	M	M	N

3.1.21 Tris(dibutylamino)cyclopropenium bromide, $[C_3(NBu_2)_3]Br$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–32	–	–	–	–	281	318

3.1.22 Tris(dipentylamino)cyclopropenium chloride, $[C_3(NPent_2)_3]Cl$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–53	–	–	–	–	261	305

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	M	M	M	M	M	N

3.1.23 Tris(dipentylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NPent_2)_3]TFSA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–73	–	–	4	5.1	343	395

T / °C	20	30	40	50	60	70	80	90
η / mPa s	269	158	97.1	62.1	41.9	29.3	21.3	16.1
σ / mS cm^{-1}	0.25	0.42	0.67	1.01	1.45	2.00	2.67	3.45
ρ / g mL^{-1}	1.086	1.079	1.072	1.064	1.057	1.050	1.043	1.036

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	M	M	M	M	M	<0.8:1 M >0.9:1 N

3.1.24 Tris(dipentylamino)cyclopropenium dicyanamide, $[C_3(NPent_2)_3]DCA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–64	–	–	–	–	292	321

T / °C	20	30	40	50	60	70	80	90
η / mPa s	308	168	97.9	60.9	40	27	19.8	14.4
σ / mS cm^{-1}	0.30	0.54	0.91	1.44	2.14	3.03	4.12	5.40
ρ / g mL^{-1}	0.927	0.921	0.915	0.909	0.903	0.897	0.891	0.885

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	M	M	M	M	M	<0.7:1 M >0.8:1 N

3.1.25 Tris(dihexylamino)cyclopropenium chloride, $[C_3(NHex_2)_3]Cl$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–54	–	–	–	–	261	300

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	M	M	M	M	M	<2:1 M >3:1 N

3.1.26 Tris(dihexylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NHex_2)_3]TFSA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–71	–	–	3	17	346	406

T / °C	20	30	40	50	60	70	80	90
η / mPa s	273	159	99.6	65.3	44.9	32.4	23.6	17.8
σ / mS cm^{-1}	0.14	0.23	0.35	0.51	0.71	0.97	1.26	1.60
ρ / g mL^{-1}	1.059	1.051	1.044	1.037	1.030	1.022	1.015	1.008

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	M	M	M	M	M	<2:1 M >3:1 N

3.1.27 Tris(dihexylamino)cyclopropenium dicyanamide, $[C_3(NHex_2)_3]DCA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–64	–	–	–	–	291	321

T / °C	20	30	40	50	60	70	80	90
η / mPa s	332	183	109	69.4	47	32.9	23.5	17.8
σ / mS cm^{-1}	0.16	0.26	0.41	0.62	0.89	1.23	1.64	2.13
ρ / g mL^{-1}	0.915	0.909	0.903	0.897	0.891	0.885	0.879	0.873

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	M	M	M	M	M	<1:1 M >2:1 N

3.1.28 Tris(dihexylamino)cyclopropenium dibutylphosphate, $[C_3(NHex_2)_3]DBP$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–60.8	–	–	–	–	223[b]	266[b]

T / °C	20	30	40	50	60	70	80	90
η / mPa s [b]	227	126	73.0	45.6	30.2	21.5	15.2	11.3
σ / mS cm^{-1} [b]	0.10	0.18	0.30	0.47	0.70	0.99	1.35	1.79
ρ / g mL^{-1} [b]	0.921	0.915	0.908	0.902	0.895	0.888	0.882	0.875

Miscibility	H_2O	MeOH	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	M	M	M	M	M	M	M

3.1.29 Tris(didecylamino)cyclopropenium chloride, $[C_3(NDec_2)_3]Cl$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–	36	7.9	45	12	259	293

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	M	M	M	M	M	M

[b] Carried out by Niels Duijvesteijn, under supervision

3.1.30 Tris(didecylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NDec_2)_3]TFSA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–	–	–	8	70	349	401

T / °C	20	30	40	50	60	70	80	90
η / mPa s	408	227	132	84.6	56	38.4	27.2	20
σ / mS cm^{-1}	0.03	0.05	0.08	0.13	0.20	0.29	0.40	–
ρ / g mL^{-1}	0.991	0.984	0.977	0.970	0.964	0.957	0.950	0.943

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	M	M	M	M	M	M

3.1.31 Tris(didecylamino)cyclopropenium dicyanamide, $[C_3(NDec_2)_3]DCA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–	–34	4.1	–13	16	276	321

T / °C	20	30	40	50	60	70	80	90
η / mPa s	554	291	163	97.5	62.3	41.6	28.9	20.8
σ / mS cm^{-1}	0.02	0.04	0.08	0.13	0.21	0.31	0.44	–
ρ / g mL^{-1}	0.890	0.884	0.878	0.872	0.866	0.860	0.854	0.849

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	M	M	M	M	M	M

3.1.32 Tris(diallylamino)cyclopropenium chloride, $[C_3(NAllyl_2)_3]Cl$

T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
227	286

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	M	M	M	M	N	M	N

3.1.33 Tris(diallylamino)cyclopropenium bromide, $[C_3(NAllyl_2)_3]Br$

T_{decomp} / °C (1°C min^{-1})	T_{decomp} / °C (10°C min^{-1})
222	241

3.1.34 Tris(diallylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NAllyl_2)_3]TFSA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–81	–	–	9	3.3	278	306

T / °C	20	30	40	50	60	70	80	90
η / mPa s	126	72.6	45.5	30.8	21.1	15.3	11.4	8.6
σ / mS cm^{-1} [c]	0.93	1.47	2.19	3.10	4.16	5.42	6.83	8.40
ρ / g mL^{-1}	1.250	1.242	1.233	1.225	1.216	1.208	1.199	1.191

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	M	M	M	M	<3:1 M >4:1 N	<0.2:1 M >0.3:1 N

3.1.35 Tris(diallylamino)cyclopropenium dicyanamide, $[C_3(NAllyl_2)_3]DCA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–68	–	–	24	8.4	235	270

T / °C	20	30	40	50	60	70	80	90
η / mPa s	211	113	65.3	41.1	27.2	19.3	15.2	10.7
σ / mS cm^{-1} [c]	0.88	1.56	2.53	3.82	5.42	7.35	9.24	–
ρ / g mL^{-1}	1.027	1.021	1.015	1.008	1.002	0.996	0.989	0.983

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	0.1:1 M >0.2:1 N	M	M	M	<1:1 M >2:1 N	<1:1 M >2:1 N	N

3.1.36 Tris(piperidino)cyclopropenium tetrafluoroborate, $[C_3(NC_5H_{10})_3]BF_4$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–	–	–	126	50	–	333[d]

[c] Carried out by Leonardus Ratten

3.1.37 Tris(piperidino)cyclopropenium nitrate, $[C_3(NC_5H_{10})_3]NO_3$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–	–	–	86	–	253	273[d]

3.1.38 Tris(diethanolamino)cyclopropenium chloride, $[C_3(N(C_2H_4OH)_2)_3]Cl$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–42	–	–	–	–	190	226

3.2 *C*$_{3h}$ cations

3.2.1 Tris(butylmethylamino)cyclopropenium chloride, $[C_3(NBuMe)_3]Cl$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–	–	–	80	21	262	293

Solubility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	S	S	S	S	N	S	N

3.2.2 Tris(butylmethylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NBuMe)_3]TFSA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–81	–	–	–	–	349	398

T / °C	20	30	40	50	60	70	80	90
η / mPa s	101	61.9	39.8	26.8	19	13.9	10.6	8.2
σ / mS cm^{-1}	0.94	1.45	2.07	2.83	3.71	4.72	5.87	7.12
ρ / g mL^{-1}	1.224	1.216	1.207	1.199	1.191	1.183	1.174	1.166

Miscibility	H_2O[d]	EtOH[d]	CH_2Cl_2[d]	EtOAc[d]	Et_2O[d]	Toluene	Hexane[d]
	N	M	M	M	M	<2:1 M >3:1 N	N

[d] Carried out by Ruomeng Wang

3.2.3 Tris(butylmethylamino)cyclopropenium dicyanamide, $[C_3(NBuMe)_3]DCA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–73	–	–	–	–	298	331

T / °C	20	30	40	50	60	70	80	90
η / mPa s	101	58.6	36.6	24.1	16.9	12.4	9.47	7.3
σ / mS cm^{-1}	1.92	3.09	4.56	6.35	8.48	10.90	13.62	16.60
ρ / g mL^{-1}	0.983	0.977	0.970	0.964	0.958	0.952	0.947	0.941

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	0.1:1 M	M	M	M	<1:1 M	<1:1 M	N
	>0.2:1 N				>2:1 N	>2:1 N	

3.2.4 Tris(butylmethylamino)cyclopropenium tetrafluoroborate, $[C_3(NBuMe)_3]BF_4$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–62	–	–	–	–	332	374

T / °C	20	30	40	50	60	70	80	90
η / mPa s[a]	360	184	102	60.8	39.9	28	20.5	14.8
σ / mS cm^{-1}	0.25	0.53	0.93	1.49	2.25	3.20	4.36	5.69

Miscibility	H_2O[d]	EtOH	CH_2Cl_2[d]	EtOAc[d]	Et_2O[d]	Toluene	Hexane[d]
	N	M	M	M	N	<2:1 M	N
						>3:1 N	

3.2.5 Tris(butylmethylamino)cyclopropenium nitrate, $[C_3(NBuMe)_3]NO_3$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–55	–	–	24	8.8	258	291

T / °C	20	30	40	50	60	70	80	90
η / mPa s [a]	392	199	108	64.4	40.8	27	19	14

Miscibility	H_2O[d]	EtOH[d]	CH_2Cl_2[d]	EtOAc[d]	Et_2O[d]	Toluene	Hexane[d]
	M	M	M	M	<0.6:1 M	<2:1 M	N
					>0.7:1 N	>3:1 N	

3.2.6 Tris(butylmethylamino)cyclopropenium thiocyanate, $[C_3(NBuMe)_3]SCN$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–69	–	–	–	–	275	308

3.2.7 Tris(octadecylmethylamino)cyclopropenium chloride, $[C_3(NC_{18}Me)_3]Cl$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–	–	–	52	52	244	278

Solubility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	S	S	N	N	N	N

3.2.8 Tris(octadecylmethylamino)cyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NC_{18}Me)_3]TFSA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
	38	11	64	39	338	384
	48	12				

Solubility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	N	S	N	N	S	N

3.2.9 Tris(octadecylmethylamino)cyclopropenium dicyanamide, $[C_3(NC_{18}Me)_3]DCA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–	–	–	52	96	241	279

Solubility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	N	S	N	N	N	N

3.3 C_{2v} cations

3.3.1 Bis(diethylamino)dimethylaminocyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2NMe_2]TFSA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–	–38	1.8	17	21	340	379
	–31	6.2				

T / °C	20	30	40	50	60	70	80	90
η / mPa s	83.6	52.4	35.2	24.7	17.9	13.4	10.3	8.2
σ / mS cm^{-1}	1.57	2.25	3.10	4.11	5.26	6.55	7.93	9.37
ρ / g mL^{-1}	1.308	1.299	1.291	1.282	1.273	1.264	1.256	1.247

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	M	M	M	<1:1 M >2:1 N	<1:1 M >2:1 N	N

3.3.2 Bis(diethylamino)dimethylaminocyclopropenium dicyanamide, $[C_3(NEt_2)_2NMe_2]DCA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–85	–	–	32	24	293	322

T / °C	20	30	40	50	60	70	80	90
η / mPa s	58.4	37.1	25.4	17.9	13.2	10	7.94	6.4
σ / mS cm^{-1}	4.64	6.97	9.54	12.44	15.70	19.25	23.13	27.21
ρ / g mL^{-1}	1.023	1.017	1.010	1.004	0.998	0.992	0.986	0.980

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	M	M	M	M	N	N	N

3.3.3 Bis(diethylamino)dibutylaminocyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2NBu_2]TFSA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–86	–	–	–4	36	355	403

T / °C	20	30	40	50	60	70	80	90
η / mPa s	126	76.4	49.9	32.7	23.1	17.2	13.0	9.9
σ / mS cm^{-1}	0.85	1.29	1.85	2.53	3.35	4.28	5.35	6.52
ρ / g mL^{-1}	1.216	1.208	1.200	1.191	1.183	1.175	1.167	1.159

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	M	M	M	<2:1 M >3:1 N	<1:1 M >2:1 N	<0.3:1 M >0.4:1 N

3.3.4 Bis(diethylamino)dibutylaminocyclopropenium dicyanamide, $[C_3(NEt_2)_2NBu_2]DCA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–81	–	–	30	28	302	334

T / °C	20	30	40	50	60	70	80	90
η / mPa s	105	63.3	40.8	27.4	19.4	14.2	11	8.6
σ / mS cm^{-1}	2.20	3.42	4.91	6.70	8.79	11.16	13.82	16.71
ρ/g mL^{-1}	0.980	0.974	0.968	0.962	0.955	0.949	0.943	0.937

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	M	M	M	<0.5:1 M >0.6:1 N	<1:1 M >2:1 N	N

3.3.5 Bis(diethylamino)dihexylaminocyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2NHex_2]TFSA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–81	–	–	–	–	356	396

T / °C	20	30	40	50	60	70	80	90
η / mPa s	182	108	67.8	44.2	30.2	21.7	15.8	12.0
ρ / g mL^{-1}	1.171	1.163	1.155	1.147	1.139	1.131	1.123	1.115

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	M	M	M	M	<2:1 M >3:1 N	<0.5:1 M >0.6:1 N

3.3.6 Bis(diethylamino)dihexylaminocyclopropenium dicyanamide, $[C_3(NEt_2)_2NHex_2]DCA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–80	–	–	–	–	304	348

T / °C	20	30	40	50	60	70	80	90
η / mPa s	131	76.8	48.4	32	22.2	16	12	9.3
σ / mS cm^{-1}	1.03	1.71	2.57	3.64	4.94	6.46	8.21	10.16
ρ / g mL^{-1}	0.958	0.952	0.946	0.939	0.933	0.927	0.922	0.916

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	M	M	M	<1:1 M >2:1 N	M	<0.4:1 M >0.5:1 N

3.3.7 Bis(diethylamino)diallylaminocyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2NAllyl_2]TFSA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–87	–	–	–26	9.4	292	358

T / °C	20	30	40	50	60	70	80	90
η / mPa s [e]	111	67.4	43.7	29.6	20.9	15.3	11.7	9.0
ρ / g mL^{-1}	1.270	1.261	1.252	1.244	1.235	1.226	1.218	1.209

3.3.8 Bis(diethylamino)diethanolaminocyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2N(C_2H_4OH)_2]TFSA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–62	–	–	–	–	235	267

T / °C	20	30	40	50	60	70	80	90
η / mPa s	–	–	249	143	89.0	58.5	40.1	28.7
σ / mS cm^{-1}	0.17	0.32	0.55	0.87	1.31	1.84	2.50	3.28
ρ / g mL^{-1}	1.256	1.247	1.239	1.230	1.222	1.214	1.206	1.198

3.3.9 Bis(diethylamino)diethanolaminocyclopropenium dicyanamide, $[C_3(NEt_2)_2N(C_2H_4OH)_2]DCA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–50	–	–	80	33	176	217

Solubility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	S	S	S	N	N	N	N

3.3.10 Bis(diisopropylamino)dibutylaminocyclopropenium chloride, $[C_3(N^iPr_2)_2NBu_2]Cl$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–6	–	–	119	33	262	292

Solubility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	S	S	S	N	N	N	N

[e] Carried out by Michael Holmes

3.3.11 Bis(diisopropylamino)dibutylaminocyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(N^iPr_2)_2NBu_2]TFSA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–	–	–	52	28	290	342

3.3.12 Bis(diisopropylamino)dibutylaminocyclopropenium dicyanamide, $[C_3(N^iPr_2)_2NBu_2]DCA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–53	–	–	47	25	302	332

3.4 *Cs* cations

3.4.1 Bis(diethylamino)butylmethylaminocyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2NBuMe]TFSA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–89	–	–	–	–	341	384

T / °C	20	30	40	50	60	70	80	90
η / mPa s	106	66.4	43.3	29.7	21.1	15.5	11.9	9.1
σ / mS cm^{-1}	1.23	1.84	2.51	3.35	4.32	5.41	6.63	7.96
ρ / g mL^{-1}	1.260	1.251	1.243	1.235	1.226	1.218	1.209	1.201

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	M	M	M	<1:1 M >2:1 N	<1:1 M >2:1 N	N

3.4.2 Bis(diethylamino)butylmethylaminocyclopropenium dicyanamide, $[C_3(NEt_2)_2NBuMe]DCA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–83	–	–	8	18	287	332

T / °C	20	30	40	50	60	70	80	90
η / mPa s	73.7	45.8	30.2	20.8	15.3	11.5	8.9	7.1
σ / mS cm^{-1}	3.50	5.12	7.13	9.50	12.20	15.24	18.60	22.16
ρ / g mL^{-1}	0.999	0.993	0.987	0.981	0.975	0.969	0.963	0.957

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	<0.5:1 M >0.6:1 N	M	M	M	<1:1 M >2:1 N	<1:1 M >2:1 N	N

3.4.3 Bis(diethylamino)hexylaminocyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2NHexH]TFSA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–78	–	–	–	–	327	371

T / °C	20	30	40	50	60	70	80	90
η / mPa s	171	103	61.3	40.8	27.9	20.4	15.2	11.4

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	M	M	M	M	<2:1 M >3:1 N	N

3.4.4 Bis(diethylamino)hexylmethylaminocyclopropenium bis(trifluoromethanesulfonyl)amide, $[C_3(NEt_2)_2NHexMe]TFSA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–86	–	–	–	–	351	398

T / °C	20	30	40	50	60	70	80	90
η / mPa s	102	62.8	41.4	28.3	20.3	15.2	11.6	9.1
σ / mS cm^{-1}	1.18	1.82	2.65	3.69	4.94	6.38	8.03	–
ρ / g mL^{-1}	1.228	1.220	1.211	1.203	1.195	1.187	1.178	1.170

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	N	M	M	M	<2:1 M >3:1 N	<1:1 M >2:1 N	<0.3:1 M >0.4:1 N

3.4.5 Bis(diethylamino)hexylmethylaminocyclopropenium dicyanamide, $[C_3(NEt_2)_2NHexMe]DCA$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–82	–	–	–	–	301	342

T / °C	20	30	40	50	60	70	80	90
η / mPa s	86.2	52.8	34.4	23.4	17	12.7	9.78	7.71
σ / mS cm^{-1}	2.77	4.34	6.34	8.82	11.75	15.13	18.88	–
ρ / g mL^{-1}	0.984	0.978	0.972	0.966	0.960	0.954	0.948	0.942

Miscibility	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	Hexane
	<0.2:1 M >0.3:1 N	M	M	M	<1:1 M >2:1 N	<2:1 M >3:1 N	<0.2:1 M >0.3:1 N

3.5 Ionic liquid fluorides

3.5.1 Tris(dipropylamino)cyclopropenium fluoride diethanol, $[C_3(NPr_2)_3]F.1.9EtOH$

T_{decomp} / °C (10°C min^{-1})
50

T / °C	20	25	30	35	40	45	50
η / mPa s	49.6	40.3	32.7	26.8	22.1	18.1	15.4
σ / mS cm^{-1}	1.89	2.28	2.74	3.24	3.75	–	–

3.5.2 Tris(diethanolamino)cyclopropenium fluoride, $[C_3(N(C_2H_4OH)_2)_3]F$

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}	T_{decomp} / °C (1 °C min^{-1})	T_{decomp} / °C (10 °C min^{-1})
–	–	–	83	–	159	191

3.5.3 Trimethylethanolammonium fluoride hydrate, $[NMe_3(C_2H_4OH)]F.H_2O$

T_{decomp} / °C (10°C min^{-1})
139

3.5.4 1-ethyl-3-methylimidazolium fluoride acetic acid, [EMIM]F.1.01AcOH

T / °C	20	25	30	35	40	45	50
η / mPa s	30.2	24.7	–	17.2	14.7	12.7	11.1
σ / mS cm^{-1}	9.37	10.8	12.4	14.3	16.2	–	–
ρ / g mL^{-1}	1.125	1.122	1.118	1.115	1.112	1.108	1.105

3.5.5 1-ethyl-3-methylimidazolium fluoride acetic acid, [EMIM]F.1.57AcOH

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}
–92	–	–	–	–

T / °C	20	25	30	35	40	45	50
η / mPa s	20.5	17.1	14.8	12.7	11.1	9.71	8.58
σ / mS cm^{-1}	11.7	–	14.8	17.0	19.1	–	–
ρ / g mL^{-1}	1.121	1.117	1.114	1.110	1.107	1.103	1.100

3.5.6 1-ethyl-3-methylimidazolium fluoride acetic acid, [EMIM]F.2.08AcOH

T / °C	20	25	30	35	40	45	50
η / mPa s	17.6	14.8	12.7	11.0	9.61	8.45	7.47
σ / mS cm^{-1}	10.8	12.5	14.3	16.2	18.6	–	–
ρ / g mL^{-1}	1.120	1.116	1.112	1.109	1.105	1.101	1.098

3.5.7 1-ethyl-3-methylimidazolium fluoride acetic acid, [EMIM]F.2.44AcOH

T / °C	20	25	30	35	40	45	50
η / mPa s	17.6	14.8	12.7	11.0	9.61	8.45	7.47
σ / mS cm^{-1}	10.6	11.9	13.4	14.9	16.6	–	–

3.5.8 1-ethyl-3-methylimidazolium fluoride acetic acid, [EMIM]F.3.22AcOH

T_g / °C	$T_{s\text{-}s}$ / °C	ΔH / kJ mol^{-1}	T_m / °C	ΔH_{fus} / kJ mol^{-1}
–95	–	–	–	–

T / °C	20	25	30	35	40	45	50
η / mPa s	13.8	11.8	10.1	8.82	7.73	6.81	6.03
σ / mS cm^{-1}	10.0	11.5	13.0	14.7	16.4	–	–
ρ / g mL^{-1}	1.118	1.114	1.110	1.106	1.102	1.098	1.094

Chapter 4

4 Synthesis of Triaminocyclopropenium salts

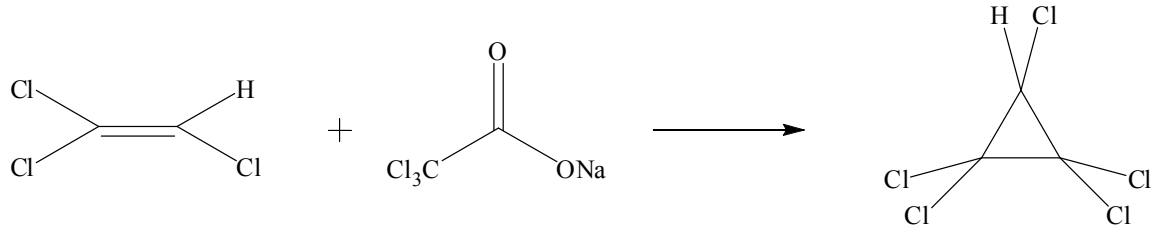
4.1 Introduction

The synthetic routes to triaminocyclopropenium salts are based on those of Yoshida[1] and Taylor,[2] as they are straightforward, easily scalable, have high yields and the starting materials are inexpensive. The resulting chloride salts can easily undergo anion metathesis with group 1 metal salts, or anion exchange with strong acids. This provides access to a wide range of anions that are non-coordinating and have dispersed charge – anions which are commonly used in ionic liquids.

Throughout this work, the synthetic method has been varied to find possible improvements and because the wide range of properties of the triaminocyclopropenium salts requires different methods for their preparation and isolation. This chapter describes the preparation of a number of triaminocyclopropenium salts that demonstrate the various synthetic routes. Both highly symmetric (D_{3h} and C_{3h}) and less symmetric (C_{2v} and C_s) examples will be covered. Unsuccessful methods will also be discussed.

4.1.1 Pentachlorocyclopropane starting material

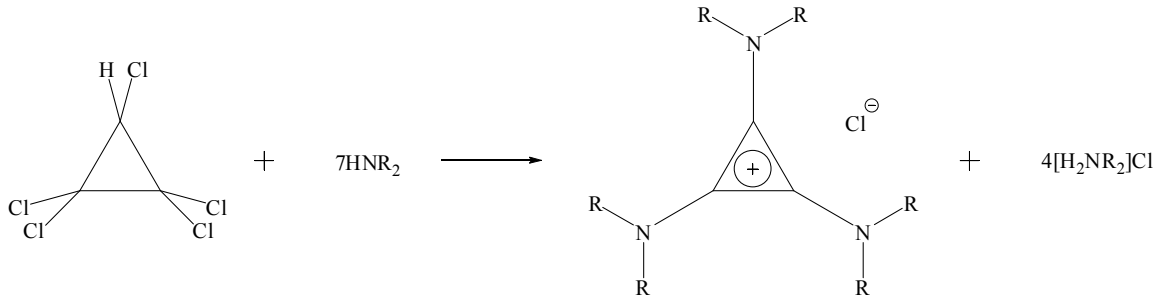
Pentachlorocyclopropane can be obtained commercially, but only on a small scale. It can, however, be prepared from a cheletropic ([1+2] cycloaddition) reaction between dichlorocarbene (generated from sodium trichloroacetate) and trichloroethene,[3] Scheme 1, which are both cheaply available on large scale, although the yield is not high (20 to 40%). Pentachlorocyclopropane was synthesized regularly on 100–200 g scale.



Scheme 1 – Synthesis of pentachlorocyclopropane

4.2 Synthesis of D_{3h} and C_{3h} symmetric cations

In 1971, Yoshida and Tawara[1] published a synthesis of tris(dialkylamino)cyclopropenium salts from tetrachlorocyclopropene and dialkylamine. Due to the basicity of dialkylamines, Taylor *et al.*[2] found that dialkylamines dehydrohalogenate pentachlorocyclopropane, and, therefore, it is possible to react dialkylamines directly with pentachlorocyclopropane to synthesize triaminocyclopropenium salts (Scheme 2).



Scheme 2 – Synthesis from pentachlorocyclopropane

The reaction in Scheme 2 was used to prepare a number of triaminocyclopropenium salts with D_{3h} and C_{3h} symmetry. Both Yoshida's and Taylor's method add the pentachlorocyclopropane to dichloromethane and stir at 0 °C under an inert atmosphere. All reagents were dried to avoid potential side reactions involving water. Temperature control of this reaction is necessary due to it being exothermic and excessive discolouration was observed if this was not done. The dialkylamine, in excess, was then added dropwise. This method was used for $[C_3(NAllyl_2)_3]Cl$, with the product isolated as a yellow liquid in good yield (89%).

A slight modification to this method was to reverse the order of addition of pentachlorocyclopropane and dialkylamine. This resulted in ionic liquids which were less coloured. When the order of addition is switched, the dialkylamine is always in excess throughout the reaction and pentachlorocyclopropane reacts straight away to the tris(dialkylamino)cyclopropenium, meaning that intermediates that are prone to side reactions (i.e. generate coloured impurities) were not present for as long. The coloured

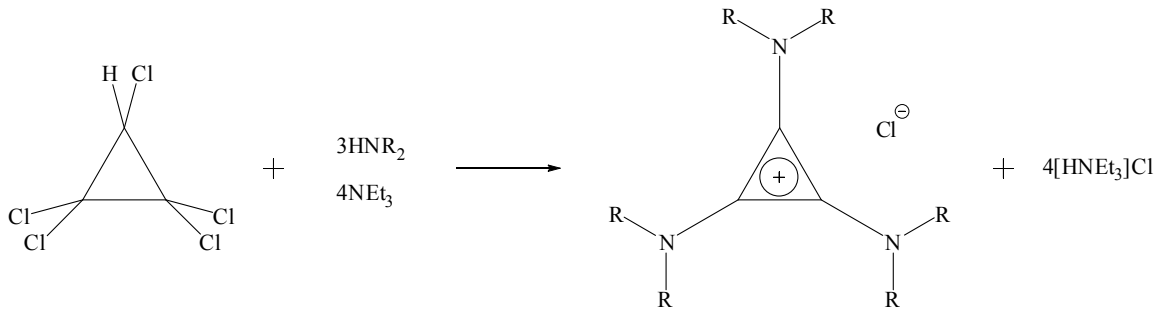
impurites were never detectable, other than visually, or observed to affect properties, but less colour is still desirable. It has often been the case with ionic liquids that they are coloured, despite analyticial techniques showing them to be pure.[4]

The reversed order of addition was used to prepare $[C_3(NMe_2)_3]Cl$, $[C_3(NEt_2)_3]Cl$, $[C_3(NPr_2)_3]Cl$, $[C_3(NBu_2)_3]Cl$ and $[C_3(NBuMe)_3]Cl$, with up to 77 g of product isolated and yields ranging from 54 to 95%. The reaction between pentachlorocyclopropane and dialkylamine was nearly quantitative, with most of the lost yield occurring during removal of the dialkylammonium salt.

In Scheme 2, the HCl generated was mopped up by excess dialkylamine, to form dialkylammonium chloride. This was undesirable if the dialkylamine was limited, if attempting a stepwise synthesis of lower symmetry triaminocyclopropenium salts or if the dialkylammonium chloride salt was difficult to remove. Therefore, a second base was added to the reaction between pentachlorocyclopropane and three equivalents of dialkylamine, as outlined in Scheme 3. Triethylamine was used since it is unable to be a substituent on the cyclopropenium cations and the triethylammonium chloride by-product is easily separated along with any dialkylammonium chloride.

Triethylamine was added with the dialkylamine to dichloromethane, followed by addition of pentachlorocyclopropane. Due to the basicity of NEt_3 (pK_a = 10.6) being similar to that of dialkylamines, excess NEt_3 was used to keep the equilibrium away from dialkylammonium chloride and towards triethylammonium chloride. $[C_3(NPent_2)_3]Cl$, $[C_3(NHex_2)_3]Cl$, $[C_3(NDec_2)_3]Cl$ and $[C_3(NC_{18}Me)_3]Cl$ were synthesized by the reaction of pentachlorocyclopropane and the respective dialkylamine with the addition of triethylamine. Up to 12 g of product was isolated, in yields of 74 to 90%.

Other bases (K^tBuO, NaH and DBU) were used during the attempted synthesis of less symmetric triaminocyclopropenium salts, and will be discussed later in this chapter.



Scheme 3 – Synthesis from pentachlorocyclopropane with additional base

4.2.1 Removal of dialkylamine/ammonium salts

For the small, volatile amines dimethyl-, diethyl-, dipropyl- and diallyl-amine, residual dialkylamine and dichloromethane were removed under vacuum to yield a mixture of the respective triaminocyclopropenium and dialkylammonium salts. However for the larger, less volatile dibutyl- and butylmethyl-amine, vacuum proved insufficient and washes with petroleum ether or diethyl ether were required to remove those dialkylamines. With the larger dipentyl-, dihexyl- and didecyl-amine removal by vacuum was not attempted and instead the reaction mixture was acidified with hydrochloric acid to convert the dialkylamine to dialkylammonium chloride, which was then removed by extraction with water. The previously mentioned small dialkylamines could have been acidified as well, but the addition of hydrochloric acid then requires multiple washes of the organic layer to remove any residual acid. This is problematic for small triaminocyclopropenium salts, which can be more water soluble than organic-solvent soluble.

Separation of the triaminocyclopropenium chloride salt from the dialkylammonium (and triethylammonium chloride if used) was carried out using one or more of a number of separation methods. A number of separation methods were required due the wide range in properties, and how similar or different these properties are to the corresponding triaminocyclopropenium and dialkylammonium salts.

Often, an initial separation was carried out to remove the bulk of the dialkylammonium salt, followed by a second step to remove it completely. This first crude separation involved filtering off the solid dialkylammonium chloride precipitate. Dialkylammonium

chloride salts are often quite insoluble in dichloromethane, so much of it could be filtered off before removal of dichloromethane. Dialkylammonium chloride salts also have low solubility in acetone, therefore, this was used for a crude separation in the synthesis of $[C_3(NEt_2)_3]Cl$, $[C_3(NPr_2)_3]Cl$, $[C_3(NBu_2)_3]Cl$ and $[C_3(NBuMe)_3]Cl$.

The most commonly used separation was addition of water, followed by extraction of the triaminocyclopropenium salt with chloroform or dichloromethane, which is then washed with water to remove remaining dialkylammonium salt. This was used in nearly all syntheses of triaminocyclopropenium salts.

Another separation technique used in the synthesis of $[C_3(N^iPr_2)_2NBu_2]Cl$, is the conversion of dibutylammonium chloride to dibutylamine by washing with dilute NaOH. The dibutyl amine was then extracted with diethyl ether washes. Due to the reactivity of hydroxide anions towards triaminocyclopropenium salts and the potential for anion exchange between chloride and hydroxide, the solution was then acidified with hydrochloric acid and then washed with water to remove NaCl and any residual acid.

$[C_3(NMe_2)_3]Cl$ and dimethylammonium chloride were unable to be separated by washing a dichloromethane solution with water, as both compounds were more soluble in the aqueous layer than the organic layer. Instead, dimethylammonium chloride was precipitated in a cooled 1:2 mixture of acetonitrile/toluene.

Another cation that was synthesized was tris(diethanolamino)cyclopropenium, because it was of interest as the fluoride salt. Separation of the triaminocyclopropenium salt and diethanolammonium chloride proved very problematic, and all methods discussed above failed. Extraction or washing did not work due to their similar solubilities, and neither are soluble in organic solvents often used when separating triaminocyclopropenium and ammonium salts, such as dichloromethane, n-butanol, acetone or acetonitrile. Silica and alumina chromatography columns did not give separation between the compounds. Cation exchange chromatography also did not work, as the diethanolamine sticks to the column despite being uncharged. These methods failed because the $[C_3(N(C_2H_4OH)_2)_3]^+$

cation and the diethanolammonium or amine are very hydrophilic due to the hydrogen bonding sites. Diethanolammonium chloride is in fact a protic ionic liquid.[5]

Separation was finally achieved by absorption into molecular sieves (13X, 10 Å pore size) and washed with ethanol and methanol to remove $[C_3(N(C_2H_4OH)_2)_3]^+$, and repeated. It is thought that the separation method was successful because the pore size is too small to easily fit $[C_3(N(C_2H_4OH)_2)_3]^+$ while the smaller $[NH_2(C_2H_4OH)_2]^+$ is trapped. However, the method only had a low yield of 16%.

4.3 Synthesis of C_{2v} and C_s symmetric cations

Ionic liquid cations generally have low symmetry which discourages efficient crystal packing, thus lowering melting points. Shortening of alkyl chains is also expected to improve transport properties. In order to do this with triaminocyclopropenium ionic liquids, synthetic methods needed further development.

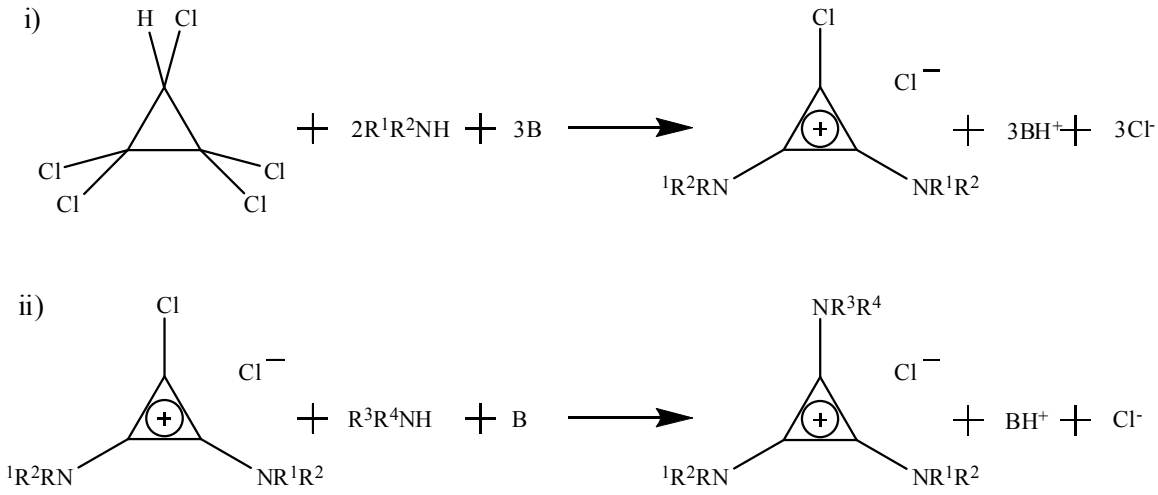
4.3.1 Stepwise routes to reduced symmetry

The first route to reduced symmetry triaminocyclopropenium cations that was investigated was a stepwise route (Scheme 4), whereby the reaction of pentachlorocyclopropane and dialkylamines was not able to go to the tri-substituted product, as only limited dialkylamine was added. It was thought that since amino groups stabilize cyclopropenium cation, the activation energy of adding another amino substituent might increase as amino substituents were added. Therefore, having limited dialkylamine present would give bis(dialkylamino)chlorocyclopropenium cations. Then, when a different dialkylamine is added, this would replace the remaining chloro substituent to form a triaminocyclopropenium salt.

The first attempt was to go via chlorobis(diethylamino)cyclopropenium, as it was thought this would be easier to stop at relative to dichloro(diethylamino)cyclopropenium. Diethylamine was used as both the nucleophile and the base, and the amine was added dropwise at 0 °C to a dichloromethane solution of pentachlorocyclopropane. The product

was found to be pure $[C_3(NEt_2)_3]^+$ cations, with a yield of 65% relative to pentachlorocyclopropane, or 98% relative to the limiting diethylamine.

In this reaction, there is the potential that any chlorobis(diethylamino)cyclopropenium formed could have undergone a disproportionation reaction during workup, forming tetrachlorocyclopropene and the observed $[C_3(NEt_2)_3]^+$ cation. This is considered unlikely to happen while the solution was cooled, as Weiss[6] only observed a disproportionation reaction of dichloro(dialkylamino)cyclopropenium to bis(dialkylamino)chlorocyclopropenium, but could have happened when the solution was heated on the rotavap during workup. Therefore, the reaction was repeated under identical conditions, however this time dibutylamine was added after diethylamine had been stirred with pentachlorocyclopropane. The product was a mixture of predominantly $[C_3(NEt_2)_3]^+$, along with $[C_3(NEt_2)_2NBu_2]^+$, $[C_3(NBu_2)_2NEt_2]^+$ and $[C_3(NBu_2)_3]^+$, showing this method is unsuitable.



Scheme 4 – Synthesis of less symmetric triaminocyclopropenium cations

In the attempted synthesis of $[C_3(NEt_2)_2NBu_2]^+$ discussed above, diethylamine was used as the base in the first step, so addition of dibutylamine would have deprotonated some diethylammonium, converting it back to diethylamine (Scheme 5), and allowing it to react with the chlorobis(diethylamino)cyclopropenium intermediate.

In the next synthesis, following the route in Scheme 4, excess triethylamine was added to pentachlorocyclopropane in dichloromethane at 0 °C, followed by two equivalents of diethylamine. After allowing the diethylamine amine to react, butylmethylamine was added. The product was a mixture of predominantly $[C_3(NEt_2)_3]^+$, along with $[C_3(NEt_2)_2NBuMe]^+$, $[C_3NEt_2(NBuMe)_2]^+$ and $[C_3(NBuMe)_3]^+$.

$$[NEt_2H_2]^+ + NBu_2H \rightleftharpoons NEt_2H + [NBu_2H_2]^+$$

Scheme 5 – Equilibrium between amine and ammonium salts

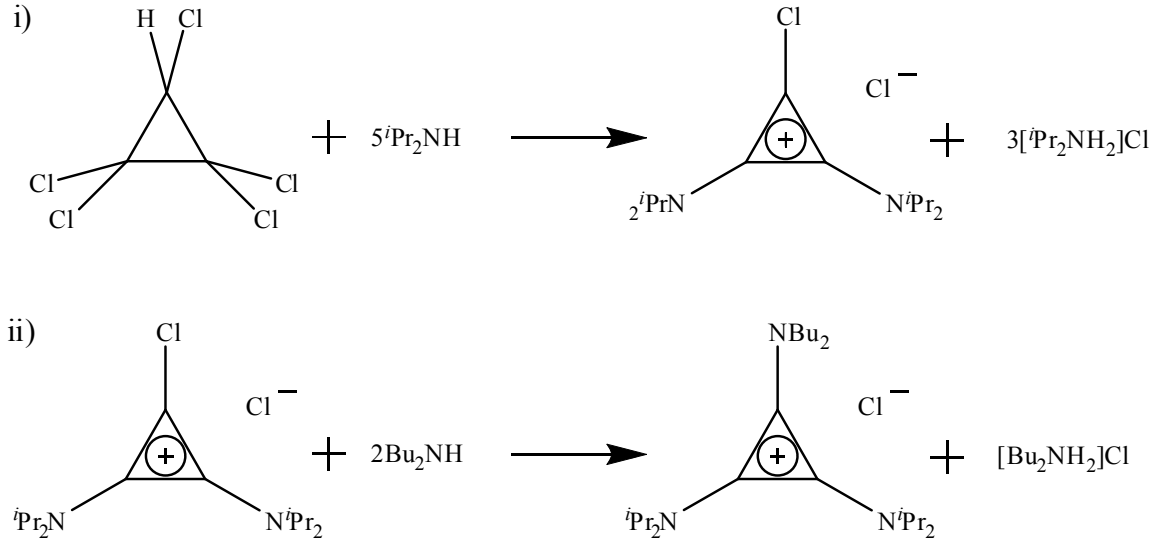
It was thought that the amino groups would stabilize the bis(dialkylamino)chlorocyclopropenium (step ii) Scheme 4) allowing this to be isolated as the activation energy for further substitution increased. To test this further, the synthesis of $[C_3(NEt_2)_2NBuMe]^+$ was attempted again using NEt_3 as the base, with the temperature lowered during addition of diethylamine to –78 °C. Again, the product was a mixture of predominantly $[C_3(NEt_2)_3]^+$, along with $[C_3(NEt_2)_2NBuMe]^+$, $[C_3NEt_2(NBuMe)_2]^+$ and $[C_3(NBuMe)_3]^+$.

The reaction outlined in Scheme 4 was also carried out using KO^{t}Bu as the base, at 0 and –78 °C, and NaH, at 0°C. In these reactions the product was a mixture of the different triaminocyclopropenium salts, predominantly $[C_3(NEt_2)_3]^+$, along with $[C_3(NEt_2)_2NBuMe]^+$, $[C_3NEt_2(NBuMe)_2]^+$ and $[C_3(NBuMe)_3]^+$ or $[C_3(NEt_2)_3]^+$, along with $[C_3(NEt_2)_2NBu_2]^+$, $[C_3(NBu_2)_2NEt_2]^+$ and $[C_3(NBu_2)_3]^+$.

While these syntheses of the less symmetric cations were unsuccessful in that they produced a mixture of compounds, the syntheses still produced triaminocyclopropenium cations, demonstrating that KO^{t}Bu and NaH could be used as the base for the synthesis of D_{3h} or C_{3h} symmetric triaminocyclopropenium cations. It was also noted that the reactions were faster using these bases. It is thought that these strong bases deprotonate the dialkylamine to a more reactive amide anion.

It was suggested that the NEt_3 may have been nucleophilically attacking the cyclopropenium intermediates, which may speed up the addition of amino substituents, allowing $[C_3(NEt_2)_3]^+$ to form instead of stopping at the chlorobis(diethylamino)cyclopropenium intermediate. Therefore a synthesis of $[C_3(NEt_2)_2NBuMe]^+$ was attempted using the non-nucleophilic base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), at –78 °C. However, the product was still a mixture of cyclopropenium compounds, $[C_3(NEt_2)_3]^+$, $[C_3(NEt_2)_2NBuMe]^+$, $[C_3NEt_2(NBuMe)_2]^+$ and $[C_3(NBuMe)_3]^+$.

In the case of bulky alkyl groups, the stepwise route can be used.[7,8] $[C_3(N^iPr_2)_2NBu_2]Cl$ was synthesized by the addition of five equivalents of diisopropylamine to pentachlorocyclopropane at 0 °C, followed by stirring at ambient temperature then addition of dibutylamine (Scheme 6). This route was successful due to the steric bulk of the isopropyl groups preventing the formation of $[C_3(N^iPr_2)_3]^+$. In order for $[C_3(N^iPr_2)_3]^+$ to form, refluxing at higher temperatures for long periods are required, and even then the yield is very low.[9]

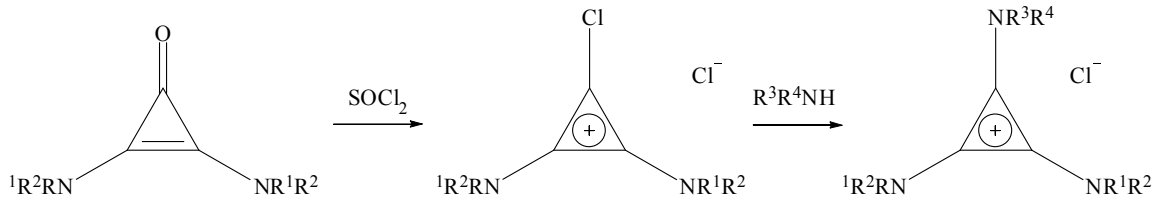


Scheme 6 – Synthesis of $[C_3(N^iPr_2)_2NBu_2]Cl$

4.3.2 Synthesis of triaminocyclopropenium cations from bis(dialkylamino)cyclopropenone

Due to the failure of the stepwise synthesis outlined in Scheme 4, another route had to be investigated. This involved preparing tris(dialkylamino)cyclopropenium salts and then reacting these with hydroxide to form bis(dialkylamino)cyclopropenones.[10] $SOCl_2$ is known to convert bis(dialkylamino)cyclopropenone to 1,2-bis(dialkylamino)-3-chlorocyclopropenium,[7] which can then be reacted with a different dialkylamine to form a triaminocyclopropenium cation (Scheme 7).

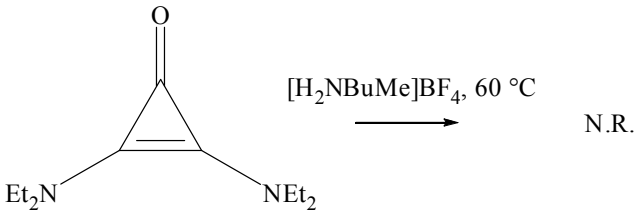
Synthesis of bis(dialkylamino)cyclopropenones will be discussed later in this chapter. Addition of thionyl chloride to bis(diisopropylamino)cyclopropenone formed the desired chloro-substituted intermediate, chlorobis(diisopropylamino)cyclopropenium chloride, in good yield. Upon addition of butylmethylamine, bis(diisopropylamino)butylmethylaminocylopropenium chloride was formed, in 50% isolated yield. The continued use of thionyl chloride was undesirable, however, due to the highly coloured product that was formed, the residual smell of the product and the hazardous nature of thionyl chloride.



Scheme 7 – Synthesis from bis(dialkylamino)cyclopropenone with thionyl chloride

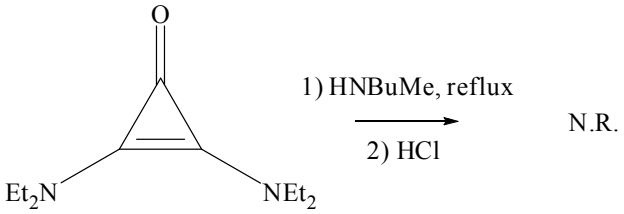
Another route to less symmetric triaminocyclopropenium salts that was investigated was the synthesis directly from bis(dialkylamino)cyclopropenone, by reaction with dialkylammonium salts, dialkylamine or dialkylamide. In the case of the ammonium salts, it was thought that the oxygen may become protonated and become an adequate leaving group to allow nucleophilic attack by the dialkylamine . Butylmethylammonium

tetrafluoroborate was mixed with bis(diethylamino)cyclopropenone and heated at 60 °C (Scheme 8), however, no reaction was observed.



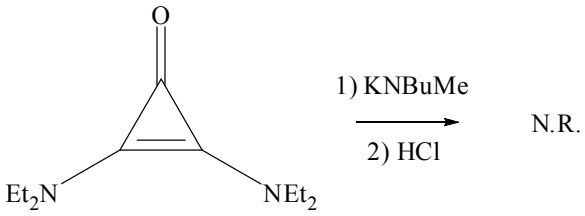
Scheme 8 – Synthesis from bis(dialkylamino)cyclopropenone with dialkylammonium salt

Likewise, butylmethylamine was refluxed with bis(diethylamino)cyclopropenone, Scheme 9, and no reaction was observed. If this reaction had been occurring it was expected that the hydroxide anion may decompose the triaminocyclopropenium cation back to a bis(dialkylamino)cyclopropenone, although this would not have resulted in pure bis(diethylamino)cyclopropenone as some amino groups would have been butylmethylamino.



Scheme 9 – Synthesis from bis(dialkylamino)cyclopropenone with dialkylamine

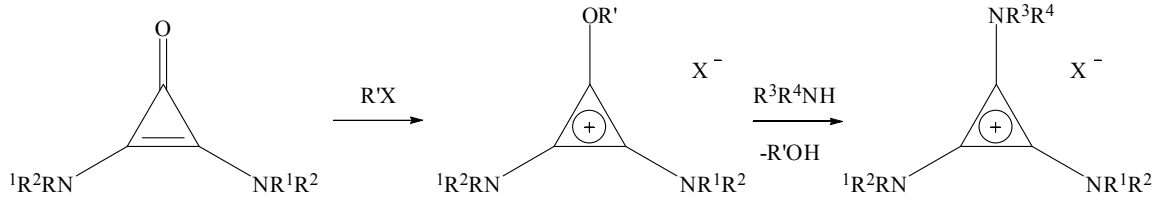
Bis(diethylamino)cyclopropenone was treated with potassium butylmethylamide (Scheme 10) and heated at 60 °C for 3 hours. No product or scrambling of amino groups was observed.



Scheme 10 – Synthesis from bis(dialkylamino)cyclopropenone with dialkylamide salt

4.3.3 Alkylation of bis(dialkylamino)cyclopropenone with iodoalkanes

In order to convert bis(dialkylamino)cyclopropenone to triaminocyclopropenium cations, it is not necessary to have a chlorine substituent attached to the reactive cyclopropenium intermediate, it is only necessary that the substituent is a leaving group readily replaced by the attacking nitrogen nucleophile. Therefore, to avoid using thionyl chloride, alkylation of the oxygen substituent in bis(dialkylamino)cyclopropenone was investigated. When the oxygen substituent is alkylated, an alkoxybis(dialkylamino)cyclopropenium cation is formed. Oxygen substituents on cyclopropenium rings do stabilize the cation, but much less so than nitrogen substituents.[7] This means that when a dialkylamine is added, this replaces the alkoxy substituent to form a triaminocyclopropenium cation (Scheme 11). The anion in the resulting salt is that of the alkylating agent used, providing an opportunity to vary the anion without an anion metathesis step. A side reaction also occurs, whereby instead of the alkoxybis(dialkylamino)cyclopropenium ring being nucleophilically attacked, the alkyl chain is, resulting in bis(dialkylamino)cyclopropenone and a trialkylammonium salt. This side reaction will be discussed later.



Scheme 11 – Synthesis from bis(dialkylamino)cyclopropenone with alkylating agent

The first alkylating agent used was iodoethane. An iodoalkane was chosen as halogen anions can be exchanged relatively easily, and iodoalkanes are better alkylating agents than other haloalkanes. Bis(diethylamino)cyclopropenone was added to excess iodoethane and heated to reflux. After removal of the iodoethane, butylmethylamine was added to give a slightly exothermic reaction and a relatively quick reaction. After removal of excess butylmethylamine, ^{1}H-NMR was then used to find the ratio of $[C_3(NEt_2)_2NBuMe]I$ to bis(dialkylamino)cyclopropenone. Usually no attempt was made to remove any ammonium salt formed, although this could have been done by dissolving in chloroform and washing with water.

With five equivalents of iodoethane and 2 h at reflux temperature, a ratio of 2.2:1 was obtained. By increasing the reaction time to 20 h, the ratio was increased to 2.4:1. An anomalous result was obtained when 2 h refluxing with twenty equivalents of iodoethane resulted in a ratio of only 0.6:1. This may have been due to water in the cyclopropenone starting material reacting with the alkoxy intermediate, forming HI acid which protonates bis(dialkylamino)cyclopropenone. Protonated bis(dialkylamino)cyclopropenone will be deprotonated by dialkylamine, rather than reacting to form triaminocyclopropenium cations. When heated to reflux for 20 h with twenty equivalents, a 4.00:1 ratio was obtained. Iodomethane proved very ineffective at alkylating bis(dialkylamino)cyclopropenone, with a ratio of only 0.2:1 obtained for ten equivalents after 20 h. Five equivalents of 2-iodopropane in 1,2-dichloroethane was heated to reflux for 16 h, and a ratio of 4.9:1 was formed.

4.3.4 Removal of residual bis(dialkylamino)cyclopropenone

The presence of residual bis(dialkylamino)cyclopropenone is problematic not just because it lowers yield, but because it is difficult to separate from the resulting ionic liquids. Bis(dialkylamino)cyclopropenone has significant zwitterionic character (Figure 4.1), making its solubility close to that of many of the desired triaminocyclopropenium salts. Separation using diethyl ether or diethyl ether/pet ether washes of the crude product were used to isolate samples of pure $[C_3(NEt_2)_2NBuMe]I$ and $[C_3(NEt_2)_2NHex_2]TFSA$. In the case of $[C_3(NEt_2)_2NHex_2]TFSA$, washes were ineffective while the anion was iodide

as the bis(diethylamino)cyclopropenone was more soluble in the ionic liquid layer. Attempts at using a cation exchange column to remove bis(diethylamino)cyclopropenone from $[C_3(NEt_2)_2NBuMe]I$ also proved ineffective. If the column was loaded with H^+, bis(diethylamino)cyclopropenone would become protonated and stick to the column. Separation on a Na^+ loaded column was possible, but yields were very low, with much of the $[C_3(NEt_2)_2NBuMe]^+$ passing through the column with bis(diethylamino)cyclopropenone, probably due to the column having a low affinity for a large organic cations.

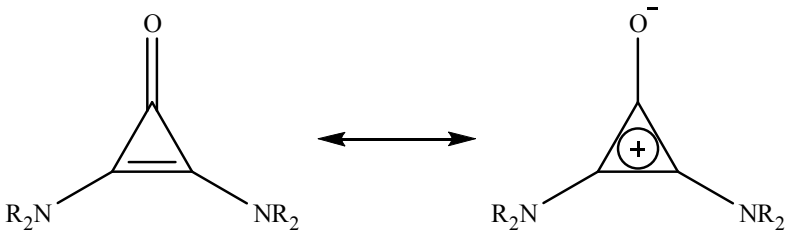


Figure 4.1 – Zwitterionic character of bis(dialkylamino)cyclopropenone

$[C_3(NEt_2)_2N(C_2H_4OH)_2]I$ was synthesized as an example of a functionalized ionic liquid. The extraction process was complicated by both $[C_3(NEt_2)_2N(C_2H_4OH)_2]I$ and the ammonium salt having similar solubilities, so a series of dichloromethane and water washes and extractions were used. First bis(diethylamino)cyclopropenone and some $[C_3(NEt_2)_2N(C_2H_4OH)_2]I$ was extracted with a dichloromethane extraction, with the $[C_3(NEt_2)_2N(C_2H_4OH)_2]I$ being recovered by extraction from the dichloromethane with water. The water fractions were combined and an extraction carried out with dichloromethane. The yield suffered, 22%, but pure $[C_3(NEt_2)_2N(C_2H_4OH)_2]I$ was obtained.

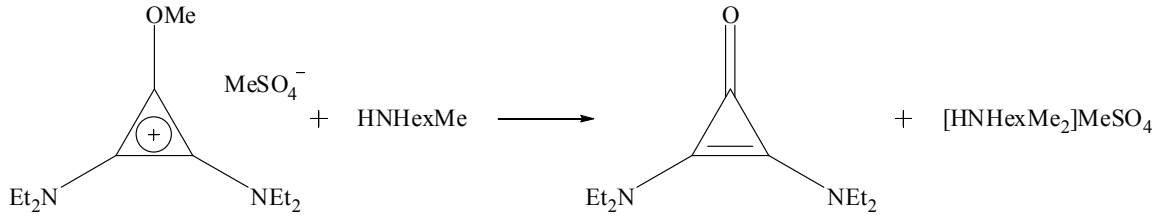
4.3.5 Alkylation of bis(dialkylamino)cyclopropenone with dimethylsulfate

Disadvantages of using iodoalkanes are the lengthy reflux times, dark brown colour of the resulting ionic liquids and only medium yields. Due to these disadvantages, dimethylsulfate was investigated as the alkylating agent. Dimethylsulfate is a much stronger alkylating agent than iodoalkanes, so was expected to form the

bis(dialkylamino)alkoxycyclopropenium intermediate in good yields, faster and without heating.

By adding two equivalents of dimethylsulfate to bis(diethylamino)cyclopropenone, ^{13}C-NMR showed the formation of bis(diethylamino)methoxycyclopropenium, in less than 15 min without heating. After addition of butylmethylamine, the intermediate bis(diethylamino)methoxycyclopropenium reacted to form $[C_3(NEt_2)_2NBuMe]^+$ in less than 5 min without heating. Small peaks for the ethyl chain of bis(diethylamino)cyclopropenone were seen. The excess dimethylsulfate and amine used meant the crude product contained a mixture of ammonium salts methylated to various degrees. These can be removed by addition of chloroform and extracted with water.

During the preparation of $[C_3(NEt_2)_2NHexMe]^+$, a ^{1}H-NMR spectrum was collected after addition of dimethylsulfate to bis(diethylamino)cyclopropenone, before the addition of hexylmethylamine. Another ^{1}H-NMR spectrum was collected after the addition of hexylmethylamine. These ^{1}H-NMR spectra showed that all of the bis(diethylamino)cyclopropenone had reacted to form bis(diethylamino)methoxycyclopropenium. However, after addition of hexylmethylamine the crude product contained 17.9 $[C_3(NEt_2)_2NHexMe]^+$: 1 bis(diethylamino)cyclopropenone. This cyclopropenone is due to a side reaction occurring, whereby instead of the bis(diethylamino)methoxycyclopropenium ring being nucleophilically attacked by hexylmethylamine, the methyl group is, which results in bis(dialkylamino)cyclopropenone and a methylated ammonium salt (Scheme 12).



Scheme 12 – Side reaction of bis(diethylamino)methoxycyclopropenium

Dimethylsulfate was used in the multigram syntheses of $[C_3(NEt_2)_2NBu_2]MeSO_4$, $[C_3(NEt_2)_2NHex_2]MeSO_4$, $[C_3(NEt_2)_2NBuMe]MeSO_4$, $[C_3(NEt_2)_2NHexMe]MeSO_4$, $[C_3(NEt_2)_2NMe_2]MeSO_4$, $[C_3(NEt_2)_2NHexH]MeSO_4$ and $[C_3(NEt_2)_2N(C_2H_4OH)_2]^+$. Bis(diethylamino)cyclopropenone was always azeotrope dried using ethanol or isopropanol, because dimethylsulfate will readily hydrolyse to methanol and methylsulfuric acid, which will protonate bis(diethylamino)cyclopropenone and prevent it from reacting with dimethylsulfate. Between 1.1 and 2 equivalents of dimethylsulfate was used in each of the reactions, with 1.1 resulting in a lower yield of 47% for $[C_3(NEt_2)_2NBu_2]MeSO_4$. $[C_3(NEt_2)_2NHex_2]MeSO_4$ and $[C_3(NEt_2)_2NHexMe]MeSO_4$ both used 1.5 equivalents of dimethylsulfate and the yield was 81.1 and 76%, which was very similar to $[C_3(NEt_2)_2NBuMe]MeSO_4$ at 79% using 2 equivalents.

Excess dimethylsulfate and dialkylamine results in the crude products containing dialkyl-, methyldialkyl- and dimethyldialkyl-ammonium salts. These were removed by addition of chloroform with the ammonium salts then extracted with water washes. Removal of bis(diethylamino)cyclopropenone from the dialkylbis(diethylamino)cyclopropenium methylsulfate was carried out by washing with diethyl ether or a diethyl ether/pet ether mixture. This was more effective than when removing bis(diethylamino)cyclopropenone from the triaminocyclopropenium iodide salts due to the different solvent environment created by the methylsulfate anions. In the case of $[C_3(NEt_2)_2NMe_2]MeSO_4$, the more polar nature of the salt resulted in the water washes (which were to remove ammonium salts) also removing some $[C_3(NEt_2)_2NMe_2]MeSO_4$, and a yield of only 38% was obtained. By adding LiTFSA to the water washes, another 28% was recovered as the TFSA salt, resulting in an overall yield of 66%.

In the case of $[C_3(NEt_2)_2NHexH]^+$, a larger excess of hexylamine was present to stop the formation of $[C_3(NEt_2)_2NHexMe]^+$. It was known that dimethylsulfate will not methylate $[C_3(NEt_2)_2NHexH]$,[11] but, if hexylamine is methylated to hexylmethylamine, then $[C_3(NEt_2)_2NHexMe]^+$ will ultimately form. During workup, hydrochloric acid was used to convert excess hexylamine to hexylammonium chloride, which could be removed, however, this meant in the resulting product there was a mixture of approximately 20%

$[MeSO_4]^-$ and 80% Cl^- anions. This is not an issue, as both anions can be exchanged for more hydrophobic anions in the same way.

Dimethylcarbonate is considered a less toxic alkylating agent, however, an attempted synthesis of $[C_3(NEt_2)_2NBuMe]^+$ using this was unsuccessful, with only the starting material bis(diethylamino)cyclopropenone being found in the product. This is likely due to dimethylcarbonate being a weak methylating agent.

Other strong alkylating agents can be used, although these were not investigated in this work. Possibilities include alkyl triflates, trifluoroacetates, tosylates or trifluoromethanesulfates. These also have the potential advantage of directly producing ionic liquids with the corresponding anions without an anion metathesis step.

4.4 Anion metathesis

Anions also play an important role in determining the properties of ionic liquids, and the use of only one anion with a range of cations could bias the observed results towards particular properties affected by the anion. In this work, a range of anions (Cl^-, TFSA, DCA, OTf, Br^-, SCN^-, NO_3^-, BF_4^-) have been used, and other students have also been expanding on this list. For TFSA, DCA, OTf and SCN^- salts, group 1 salts (sodium or lithium) have been used for the anion metathesis step. This usually involved mixing an excess of the anion group 1 metal salt with the triaminocyclopropenium chloride or methylsulfate salt in an aqueous solution. The more hydrophobic anion being introduced usually formed a separate ionic liquid layer with the triaminocyclopropenium cation, while the more hydrophilic chloride or methylsulfate anion and group 1 cation would remain in the aqueous layer. The ionic liquid was then extracted with an organic solvent such as diethyl ether, dichloromethane or chloroform. Another addition of the anion salt was usually carried out, before washing the organic solvent with water to remove any excess anion salt. Generally the yield was good, 80-90%.

In the case of bromide, NO_3^- and BF_4^- anions, the triaminocyclopropenium chloride salt was dissolved in an aqueous solution and an excess of the anion acid added. Addition of

an organic solvent would extract out the triaminocyclopropenium salt, and this could be washed multiple time with excess aqueous acid. The organic layer was then washed with water until the pH returned to neutral. Yields were usually slightly lower, 52-80%.

4.5 Impurities in ionic liquid samples

It is important to consider the effect of impurities on the ionic liquids. It is well-known that chloride anions can play an important role in determining properties.[12] Chloride is the main anion impurity in this work because the symmetric triaminocyclopropenium salts were synthesized as the chloride salt. Chloride concentration was determined using a chloride ion selective electrode: in most cases, the ionic liquid sample was dissolved into an aqueous solution, although, in some cases, ethanol was added to make the sample soluble. In most cases, the concentration of chloride ions was less than 500 ppm, which corresponds to approximately 0.5% of total anions. There were cases of higher chloride concentrations, these were often in the case of metathesis from the anion acid. Some DCA salts also have a higher than desirable concentration of chloride due to sodium chloride impurities in some of the NaDCA salt used. The highest chloride concentration was found for $[C_3(NEt_2)_2NMe_2]$DCA which had a chloride concentration of 3550 ppm (0.100 mol kg^{-1}). This corresponds to 2.9% of all anions in the sample, and will have increased the viscosity and decreased the conductivity, but probably by less than 10%. In the case of the thiocyanate anion no chloride content was able to be determined due to the interference of thiocyanate with the ion selective electrode, due to the insolubility of silver thiocyanate.

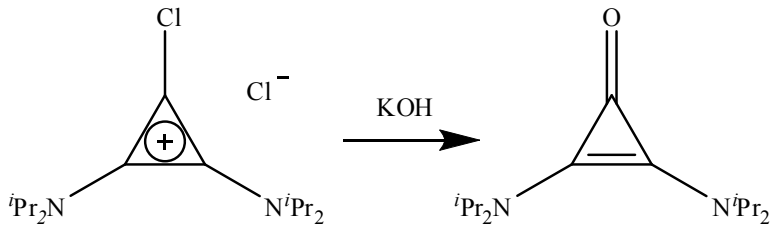
For the synthesis of triaminocyclopropenium salts via bis(dialkylamino)cyclopropenium using dimethylsulfate, ^{1}H-NMR spectroscopy showed no methylsulfate anion impurities after anion exchange. While this synthesis via cyclopropenone is a chloride free synthesis, chloride however, can still be a major impurity, entering the sample during the anion metathesis step.

The other important impurity to consider is water[12,13] This may enter a sample during workup, metathesis or from the atmosphere. While water does not degrade the samples, it

does have a major effect on properties, especially the transport properties, glass transition temperatures and melting points. Before any properties were measured the samples were dried by heating and stirring under vacuum for at least 24 hours. Water content was measured using a columbic Karl-Fischer titration. Most water contents were less than 300 ppm, although in some cases, such as thiocyanates, nitrates and DCA, water was much harder to remove due to hydrogen bonds forming between water and the anion.

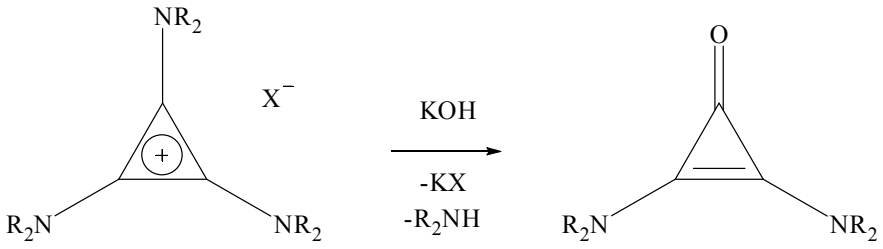
4.6 Synthesis of bis(dialkylamino)cyclopropenone

For the synthesis of C_{2v} and C_s triaminocyclopropenium salts, bis(dialkylamino)cyclopropenone was needed. 1,2-bis(diisopropylamino)cyclopropenone can be synthesized by the addition of aqueous potassium hydroxide to 1,2-chlorobis(diisopropylamino)cyclopropenium chloride,[14] Scheme 13.



Scheme 13 – Synthesis of bis(diisopropylamino)cyclopropenone

However, since in most cases the reaction will not stop at the bis(dialkylamino)chlorocyclopropenium, as discussed in the stepwise synthesis section earlier in the chapter, a more general method of synthesis is needed. In 1980, Wilcox[10] synthesized bis(dialkylamino)cyclopropenone from tris(dialkylamino)cyclopropenium salts, Scheme 14. $[C_3(NEt_2)_3]Cl$ was added to solution of potassium hydroxide and heated at 70 °C for 18 hours. While Wilcox was able to separate bis(diethylamino)cyclopropenone from unreacted $[C_3(NEt_2)_3]Cl$ via vacuum distillation, this proved unsuccessful due to inadequate vacuum, so separation was carried out via extraction with dichloromethane from the aqueous solution. Because reactions were carried out using extraction, care had to be taken that the triaminocyclopropenium salt had completely reacted which meant long reaction times. Nevertheless this reaction was carried out repeatedly, with yields in the range 70 to 80%.



Scheme 14 – Synthesis of bis(dialkylamino)cyclopropenone

An investigation into the kinetics of the reaction of tris(diethylamino)cyclopropenium and hydroxide was carried out. The reaction was carried out under similar, but not identical, conditions to the large-scale synthesis, using NaOD in a 50:50 mixture of D_2O and CD_3OD and monitored with ^{1}H-NMR for 12 h. CD_3OD had to be added to avoid formation of an organic layer of diethylamine, $[C_3(NEt_2)_3]^+$ and bis(diethylamino)cyclopropenone. In the large scale synthesis, this does not happen as diethylamine evaporates off. There were two reasons for these experiments, the first was to optimize the synthesis of bis(dialkylamino)cyclopropenone and minimize contamination with tris(dialkylamino)cyclopropenium. The second reason was that, if this reaction was shown to be an equilibrium, then the reverse reaction from bis(dialkylamino)cyclopropenone could synthesize bis(dialkylamino)-dialkylaminocyclopropenium salts.

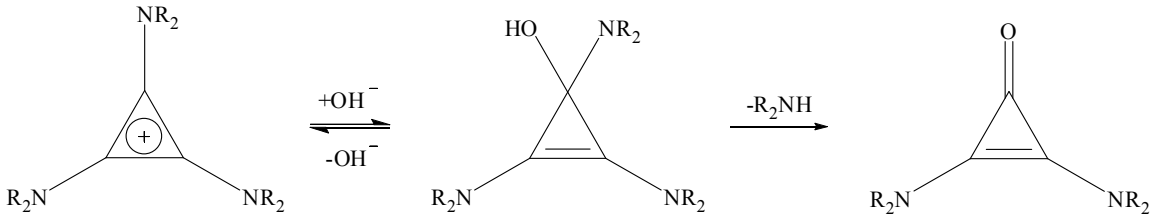
The reaction was seen to be first order with respect to $[C_3(NEt_2)_3]^+$ concentration. The order with respect to $[OD]^-$ was found numerically to be approximately 3.7. The results are summarized in Table 4-1. Using the reaction at 25 °C and an average rate constant at 50 °C of 5.44 x 10^{-6} (L mol^{-1})$^{3.7}$ s^{-1}, the activation energy was found to be 104 kJ mol^{-1} with an Arrhenius prefactor of 4.01 x 10^{11}. This relatively high activation energy (at least for a hydroxide nucleophile reacting with a cation) is due to the loss of aromaticity in the transition state. One variation between these experiments not taken into account is the different ionic strengths of the solutions. The high order of reaction with respect to $[OD]^-$ shows that under low concentrations the triaminocyclopropenium cation is not extremely sensitive to nucleophilic attack by hydroxide. Triaminocyclopropenium cations also show low reactivity as the temperature is dropped. Simulations show that at 20 °C in 2.5 mol

L^{-1} NaOH, approximately only 10% of $[C_3(NEt_2)_3]^+$ has reacted within 10 h. This shows that triaminocyclopropenium solutions can be handled under basic conditions at ambient temperature for short periods of time without hydrolysis to bis(dialkylamino)cyclopropenone.

Table 4-1 – Kinetic data for synthesis of bis(diethylamino)cyclopropenone

Temperature °C	$[C_3(NEt_2)_3]^+$ mmol L^{-1}	NaOD mol L^{-1}	k' $x10^{-6}$ s^{-1}	k $x10^{-6}$ $(L\ mol^{-1})^{3.66}\ s^{-1}$
25	64.4	2.50	5.98	0.21
50	56.2	1.25	13.9	6.14
50	55.6	2.50	137	4.80
50	55.0	3.75	347	2.75
50	33.4	5.00	1740	4.81
50	171.2	2.50	171	5.99

No overall equilibrium was observed, with the reaction going to completion in all cases other than the reaction at 25 °C and the reaction using 1.25 mol L^{-1}. It is thought that the reaction between tris(dialkylamino)cyclopropenium and hydroxide occurs with an equilibrium step first, where the hydroxide nucleophilically attacks the cyclopropenium ring. This forms an intermediate species, where either the nitrogen to carbon bond, to form bis(dialkylamino)cyclopropenone, or the oxygen to carbon bond can be broken, to reform tris(dialkylamino)cyclopropenium.



Scheme 15 – Reaction of triaminocyclopropenium with hydroxide

4.7 Conclusions

The preparation of a range of triaminocyclopropenium ionic liquids has been described. D_{3h} and C_{3h} symmetric cations can be prepared from pentachlorocyclopropane and dialkylamine, with and without an additional base. The stepwise synthesis of C_{2v} and C_s symmetric cations were nearly all unsuccessful, with the products being mixtures of

triaminocyclopropenium salts. The only successful stepwise synthesis utilized bulky alkyl substituents, which prevent addition of the third dialkylamino substituent.

However, C_{2v} and C_s symmetric cations were successfully synthesized from bis(dialkylamino)cyclopropenone. Bis(dialkylamino)cyclopropenone could be converted to a bis(dialkylamino)chlorocyclopropenium cation with thionyl chloride, however, it was more desirable to convert to a bis(dialkylamino)alkoxycyclopropenium cation with an alkylating agent such as iodoethane or dimethylsulfate. Bis(dialkylamino)alkoxycyclopropenium cations readily react with dialkylamine to form triaminocyclopropenium cations.

Metathesis of the chloride, iodide or methylsulfate anions produced ionic liquids with a range of anions – TFSA, DCA, OTf, Br^-, SCN^-, NO_3^-, BF_4. These ionic liquids were characterized, paying particular attention to the water and chloride impurities.

The kinetics of the reaction of triaminocyclopropenium cations and hydroxide, which synthesizes bis(dialkylamino)cyclopropenone, was studied. The reaction was seen to be first order with respect to $[C_3(NEt_2)_3]^+$ and an order with respect to $[OD]^-$ was found numerically to be approximately 3.7. The activation energy was found to be 104 kJ mol^{-1}.

4.8 References

(1) Yoshida, Z.; Tawara, Y. *J. Am. Chem. Soc*. **1971**, *93*, 2573-2574.

(2) Taylor, M. J.; Surman, P. W. J.; Clark, G. R. *J. Chem. Soc., Chem. Commun.* **1994**, 2517-2518.

(3) Tobey, S. W.; West, R. *J. Am. Chem. Soc.* **1966**, *88*, 2478-2481.

(4) Earle, M. J.; Gordon, C. M.; Plechkova, N. V.; Seddon, K. R.; Welton, T. *Anal. Chem.* **2007**, *79*, 758-764.

(5) Zhao, C.; Burrell, G.; Torriero, A. A. J.; Separovic, F.; Dunlop, N. F.; MacFarlane, D. R.; Bond, A. M. *J. Phys. Chem. B* **2008**, *112*, 6923-6936.

(6) Weiss, R. *Tetrahedron Lett.* **1979**, *35*, 3295-3296.

(7) Yoshida, Z. *Topics in Current Chemistry* **1973**, *40*, 47-72.

(8) Clark, G. R.; Surman, P. W. J.; Taylor, M. J. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1523-1528.

(9) Butchard, J. R.; Curnow, O. J.; Pipal, R. J.; Robinson, W. T.; Shang, R. *J. Phys. Org. Chem.* **2008**, *21*, 127-135.

(10) Wilcox, C.; Breslow, R. *Tetrahedron* **1980**, *21*, 3241-3242.

(11) Yunis, R., Personal Communication, **2011**.

(12) Seddon, K. R.; Stark, A.; Torres, M. *J. Pure Appl. Chem.* **2000**, *72*, 2275-2287.

(13) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. *Green Chem.* **2001**, *3*, 156-164.

(14) Yoshida; Konishi, H.; Tawara, Y.; Qgoshi, H. *J. Am. Chem. Soc.* **1973**, *95*, 3043-3045.

Chapter 5

5 Properties of Triaminocyclopropenium ionic liquids

5.1 Introduction

In this work, a number of properties of triaminocyclopropenium ionic liquids have been investigated. Before any applications are considered, a good understanding of the properties is required. These properties include some of the physicochemical (thermal behaviour and transport properties) and stability properties (electrical, thermal and chemical).

This chapter will discuss the properties measured, the trends seen, the effects observed and what the results mean. These results will be compared with other ionic liquid data that is published in the literature to put the properties of triaminocyclopropenium ionic liquids into perspective.

5.2 DSC

Differential scanning calorimetry (DSC) looks at the heat flow into and out of a sample, as the temperature is changed. For the DSC experiments reported here, three heating and cooling cycles were carried out, and all measurements are taken off the second and third cycles, because the first cycle is often irreproducible as the sample melts and moves.

In the example below (Figure 5.1) a number of features are illustrated. At –71 °C, a glass transition temperature (T_g) is observed. At the glass transition temperature, the sample transitions from being in a frozen glass state to being in a supercooled liquid state, shown by the change in heat capacity. At –40 °C, the onset of crystallisation is observed, although this point is not repeatable as other factors affecting nucleation vary. Crystallisation can also occur on the cooling cycle, and if this occurs a glass transition temperature is not observed as the sample stays in the crystal phase. At –2 °C, a solid-solid transition ($T_{s\text{-}s}$) is observed between two different solid phases. The position and size of this peak is usually reproducible, the integral and sample size are used to calculate the enthalpy of the transition. Multiple solid-solid transitions can be observed, in some

samples three were seen. For both the solid-solid transition and the later melting point, it is the onset point that is reported as the transition temperature. At 30 °C, the final melting point (T_m) is observed, and the integral of this peak is the enthalpy of fusion. Since ΔG is 0, the enthalpy of fusion is used to calculate the entropy of fusion.

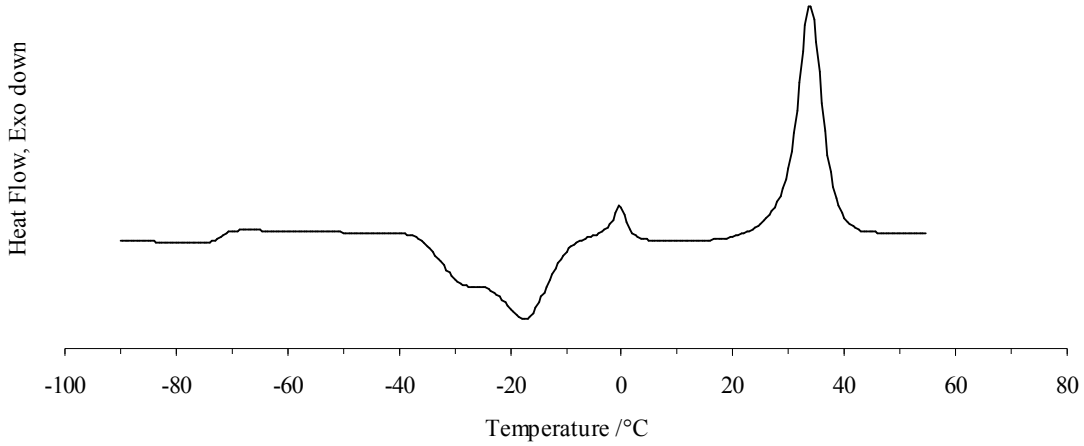


Figure 5.1 – DSC trace of $[C_3(NPr_2)_3]$TFSA

The DSC results are summarized in Table 5-1. Most of the salts have melting points that are below 100 °C, and therefore qualify as ionic liquids, with only three salts having a melting point greater than 100 °C. It is not entirely predictable as to which compounds will give a melting point and which will just give a glass transition temperature. In general, it is seen that the less symmetric cations, like those with C_s symmetry, are less likely to show melting points, instead becoming supercooled. Viscosity can also play a role in determining if a melting point is seen: if viscosity is too high the sample may not be able to crystallize, instead staying in a supercooled state. High melting point compounds were more likely to crystallize on the cooling cycle, and so did not show a glass transition temperature. It should be noted that, for the compounds where melting points were not detected, it does not mean they do not have a melting point. Under other conditions, for example slower cooling or holding at low temperatures, crystallization might be observed, after which a melting point could be observed.

When considering melting points, it is important to think about the forces involved. The dominant force in ionic salts with a high melting point is often the electrostatic attraction between ions. However, in ionic liquids the electrostatic attraction has been decreased to a similar level as other forces. Hydrogen bonds, van der Waals, aromatic stacking etc can all contribute. Coulombic energy is given by the following equation:

$$E_c = \frac{MZ^+Z^-}{4\pi\varepsilon_0 r}$$

Three factors govern the Coulombic energy, of which some, if not all, need to be changed to lower melting points. First is the Madelung constant (M) which takes into account the packing efficiency of the ions. This is decreased by ions with low symmetry or conformational equilibrium due to flexibility. The second factor is the product of the ion charges (Z), however, all the triaminocyclopropenium cations have a charge of +1, and all the anions used to have a charge of –1, so this factor does not change in this work. The third factor is the ion-ion separation (r), which decreases melting points as ion-ion separation increases. Triaminocyclopropenium cations have a delocalized charge, spread over the cyclopropenium ring and the nitrogen substituents, which effectively increases the ion-ion separation.

Table 5-1 – Summary of DSC results

		M_{cation} g mol^{-1}	T_g °C	$T_{s\text{-}s}$ °C	ΔH kJ mol^{-1}	ΔS J mol^{-1} K^{-1}	T_m °C	ΔH_{fus} kJ mol^{-1}	ΔS_{fus} J mol^{-1} K^{-1}
D_{3h}	$[C_3(NMe_2)_3]$TFSA	168	–	45	2.6	8.3	105	8.3	22
				65	1.9	5.7			
				83	2.2	6.1			
	$[C_3(NEt_2)_3]$Cl	252	–				92	16	44
	$[C_3(NEt_2)_3]$TFSA	252	–86	–34	–		19	19	65
				1	9.4	34			
	$[C_3(NEt_2)_3]$DCA	252	–	–			10	3.5	12
	$[C_3(NEt_2)_3]BF_4$	252	–	–			24	20	66
	$[C_3(NEt_2)_3]NO_3$	252	–66	–			31	5	17
	$[C_3(NEt_2)_3]$SCN	252	–77	–			–3	13.1	48
	$[C_3(NEt_2)_3]ClO_4$	252	–65	–			39	23	74
	$[C_3(NC_5H_{10})_3]BF_4$	288	–	–			126	50	125
	$[C_3(NC_5H_{10})_3]NO_3$	288	–	–			86	–	
	$[C_3(NAllyl_2)_3]$TFSA	324	–82	–			9	3.3	12
	$[C_3(NAllyl_2)_3]$DCA	324	–68	–			24	8.4	28
	$[C_3(NPr_2)_3]$Cl	336	–30	65	9.3	28	75	15	42
	$[C_3(NPr_2)_3]$TFSA	336	–71	–2	1.9	7.0	30	20	67
	$[C_3(NPr_2)_3]$DCA	336	–	–			49	26	80
	$[C_3(NPr_2)_3]BF_4$	336	–	–			77	21	61
	$[C_3(NPr_2)_3]NO_3$	336	–55	–			–		
	$[C_3(NBu_2)_3]$TFSA	420	–74	–			3	19	67
	$[C_3(NBu_2)_3]$DCA	420	–62	–			14	8.8	31
	$[C_3(NBu_2)_3]BF_4$	420	–53	–			29	19	65
	$[C_3(NBu_2)_3]NO_3$	420	–62	–			–		
	$[C_3(NBu_2)_3]$OTf	420	–58	–			42	26	81
	$[C_3(NBu_2)_3]$Br	420	–32	–			–		
	$[C_3(NPent_2)_3]$Cl	504	–53	–			–		

		M_{cation} g mol^{-1}	T_g °C	$T_{s\text{-}s}$ °C	ΔH kJ mol^{-1}	ΔS J mol^{-1} K^{-1}	T_m °C	ΔH_{fus} kJ mol^{-1}	ΔS_{fus} J mol^{-1} K^{-1}
D_{3h}	$[C_3(NPent_2)_3]TFSA$	504	–73	–			4	5.1	19
	$[C_3(NPent_2)_3]DCA$	504	–64	–			–		
	$[C_3(N(C_2H_4OH)_2)_3]Cl$	348	–82	–			–		
	$[C_3(NHex_2)_3]Cl$	588	–54	–			–		
	$[C_3(NHex_2)_3]TFSA$	588	–71	–			3	17	60
	$[C_3(NHex_2)_3]DCA$	588	–64	–			–		
	$[C_3(NHex_2)_3]DBP$	588	–60.8	–			–		
	$[C_3(NDec_2)_3]Cl$	924	–	36	7.9	25	45	13	40
	$[C_3(NDec_2)_3]TFSA$	924	–	–			8	70	250
	$[C_3(NDec_2)_3]DCA$	924	–	–34	4.1	17	–13	16	61
C_{3h}	$[C_3(NBuMe)_3]Cl$	294	–	–			80	21	60
	$[C_3(NBuMe)_3]TFSA$	294	–81	–			–		
	$[C_3(NBuMe)_3]DCA$	294	–73	–			–		
	$[C_3(NBuMe)_3]BF_4$	294	–62	–			–		
	$[C_3(NBuMe)_3]NO_3$	294	–55	–			24	8.8	30
	$[C_3(NBuMe)_3]SCN$	294	–69	–			–		
	$[C_3(NC_{18}Me)_3]Cl$	882	–	–			52	52	161
	$[C_3(NC_{18}Me)_3]TFSA$	882	–	38	11	34	64	39	115
				48	12	37			
	$[C_3(NC_{18}Me)_3]DCA$	882	–	–			52	96	296
C_{2v}	$[C_3(NEt_2)_2NMe_2]TFSA$	882	–	–38	1.8	7.8	17	21	71
				–31	6.2	25			
	$[C_3(NEt_2)_2NMe_2]DCA$	224	–85	–			32	24	80
	$[C_3(NEt_2)_2NAllyl_2]TFSA$	276	–87	–			–26	9.4	38
	$[C_3(NEt_2)_2NBu_2]TFSA$	308	–86	–			–4	36	133
	$[C_3(NEt_2)_2NBu_2]DCA$	308	–81	–			30	28	93

		M_{cation} g mol^{-1}	T_g °C	$T_{s\text{-}s}$ °C	ΔH kJ mol^{-1}	ΔS J mol^{-1} K^{-1}	T_m °C	ΔH_{fus} kJ mol^{-1}	ΔS_{fus} J mol^{-1} K^{-1}
C_{2v}	$[C_3(NEt_2)_2NHex_2]$TFSA	364	–81	–			–		
	$[C_3(NEt_2)_2NHex_2]$DCA	364	–80	–			–		
	$[C_3(N^iPr_2)_2NBu_2]$Cl	364	–6	–			119	33	84
	$[C_3(N^iPr_2)_2NBu_2]$TFSA	364	–	–			52	28	85
	$[C_3(N^iPr_2)_2NBu_2]$DCA	364	–53	–			47	25	78
	$[C_3(NEt_2)_2N(C_2H_4OH)_2]$TFSA	284	–62	–			–		
	$[C_3(NEt_2)_2N(C_2H_4OH)_2]$DCA	284	–50	–			80	33	94
C_s	$[C_3(NEt_2)_2NBuMe]$TFSA	266	–89	–			–		
	$[C_3(NEt_2)_2NBuMe]$DCA	266	–83	–			8	18	62
	$[C_3(NEt_2)_2NHexH]$TFSA	280	–78	–			–		
	$[C_3(NEt_2)_2NHexMe]$TFSA	294	–86	–			–		
	$[C_3(NEt_2)_2NHexMe]$DCA	294	–82	–			–		

Within the compounds synthesized, a number of effects were seen, the first being that flexible chains reduce melting points, whereas rings with reduced flexibility give higher melting points. For example this was observed in $[C_3(NC_5H_{10})_3]^+$ salts, where the tetrafluoroborate and nitrate salts had high melting points, 126 and 86 °C. $[C_3(NC_5H_{10})_3]BF_4$ does not qualify as an ionic liquid, although this definition is arbitrary. Due to the alkyl chains being joined in the piperidine ring, the flexibility has been decreased, with only a few different conformations of the ring being possible. This lack of flexibility makes it comparable to the $[C_3(NMe_2)_3]^+$, which also has a high melting point due to a lack of flexibility and small size. Branched isopropyl groups also result in higher melting points due to reduced effective flexibility.[1-3] When the $[C_3(N^iPr_2)_2NBu_2]^+$ salts are compared to $[C_3(NEt_2)_2NBu_2]^+$, which also is C_{2v} symmetry and only a slightly smaller cation, a melting point increase of 56 °C is seen for the TFSA salt and an increase of 17 °C is seen for the DCA salt, due to the extra methyl group on the α-carbon of the alkyl chain.

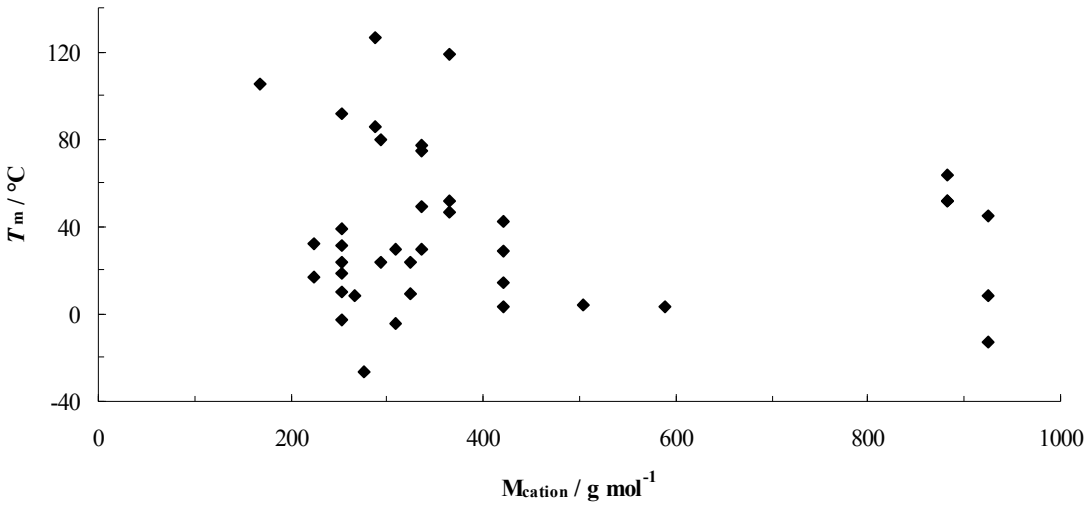


Figure 5.2 – Melting points of triaminocyclopropenium cations reported in this work

Unsaturated alkyl chains were seen to decrease melting points. When the $[C_3(NAllyl_2)_3]^+$ salts are compared to $[C_3(NPr_2)_3]^+$, a melting point decrease of 19 °C is seen for the TFSA salt and a decrease of 25 °C is seen for the DCA salt, due to the replacement of a propyl group with an allyl group. $[C_3(NEt_2)_2NAllyl_2]$TFSA is noteworthy due to the low

melting point of –26 °C, the lowest observed in this work. This can be attributed to both the lower symmetry as well as the unsaturated allyl chains, which causes repulsion between π bond electrons and the anion.

Hydrogen bonds will increase the intermolecular forces, increasing the melting point. This was seen in the case of $[C_3(NEt_2)_2N(C_2H_4OH)_2]$DCA, which has a melting point of 80 °C, the highest of any of the DCA salts.

When the melting points of only cations with straight, saturated alkyl chains are considered, we first see a general overall decrease in melting points as the molecular weight increases (Figure 5.3). For example, if the TFSA anion salts are considered, the melting point of $[C_3(NMe_2)_3]$TFSA is 105 °C, but this decreases to 3.0 °C for $[C_3(NHex_2)_3]$TFSA. This decrease in melting points is due to the dilution of charged centers and increased flexibility of long alkyl chains, which decreases efficient crystal packing and therefore decreases melting points. However, as chain length is increased further, the increased van der Waals forces between the alkyl chains will increase. In the case of other classes of ionic liquid cation the increase in van der Waal forces can often increase melting points, such as 1-alkyl-3-methylimidazolium based ionic liquids.[4] $[C_1MIM]BF_4$ melts at 103 °C, C_2 to C_9 did not show melting points, $[C_{10}MIM]BF_4$ melted at –4 °C and the melting points steadily increased after this point, with $[C_{12}MIM]BF_4$ melting at 26 °C. With triaminocyclopropenium ionic liquids, the increase is not seen – $[C_3(NDec_2)_3]$TFSA has a melting point of 8 °C, slightly higher than $[C_3(NHex_2)_3]$TFSA, and $[C_3(NDec_2)_3]$DCA has a melting point of –13 °C, the lowest melting point for a triaminocyclopropenium DCA ionic liquid. It is thought that with triaminocyclopropenium ionic liquids the increasing van der Waals forces are counteracted by a decrease in the ionicity (increase the ion pairing), decreasing the electrostatic intermolecular forces. Evidence for the decreasing ionicity is discussed later when analysing Walden plots. It should be noted that the size of the $[C_3(NDec_2)_3]^+$ cation is 925.7 g mol^{-1}, which is very large for an ionic liquid cation, much larger than $[C_{10}MIM]^+$ which is 223.4 g mol^{-1}. Melting points of –13 °C for $[C_3(NDec_2)_3]$DCA, 8 °C

for $[C_3(NDec_2)_3]$TFSA and 45 °C for $[C_3(NDec_2)_3]$Cl, are quite remarkable considering the size of the cation.

The effect of increasing alkyl chain length decreasing melting points is only a general trend, and there are exceptions in this data. When the melting points of $[C_3(NEt_2)_3]^+$ and $[C_3(NBu_2)_3]^+$ for the BF_4 and DCA salts are compared, a slightly lower melting point was observed for the shorter chain $[C_3(NEt_2)_3]^+$; although the reason for this is suspected to be the higher chloride contents in the $[C_3(NEt_2)_3]^+$ sample as the impurity will lower the melting points.

The effect of increasing alkyl chain length on decreasing melting points can also be observed in the C_{2v} symmetric series. $[C_3(NEt_2)_2NMe_2]$TFSA and DCA have melting points of 17 and 32 °C, respectively, which drop to –4 and 30 °C, respectively, for the $[C_3(NEt_2)_2NBu_2]^+$ salts.

It is interesting to note that while the overall effect of increasing chain length decreases the melting point for small cations, there is a slight alternating effect in which odd numbers of carbon atoms in a chain result in a higher melting point than even numbers. This is seen in the TFSA anion series where we have a complete set of melting points, the $[C_3(NPr_2)_3]^+$ and $[C_3(NPent_2)_3]^+$ salts are elevated relative to the neighbouring cations; although, the difference between the butyl, pentyl and hexyl chains is very small, less than the uncertainty. The chloride anion series does not follow this trend, with $[C_3(NPr_2)_3]$Cl being lower than $[C_3(NEt_2)_3]$Cl, but the hydrophilicity of chloride means there are doubts over these melting points. In the BF_4 series, $[C_3(NPr_2)_3]^+$ has a higher melting point than the neighbouring $[C_3(NEt_2)_3]^+$ or $[C_3(NBu_2)_3]^+$. This alternating sequence is also seen in a series of alkyltrioctylphosphonium ionic liquids,[5] although it is not yet explained in detail.

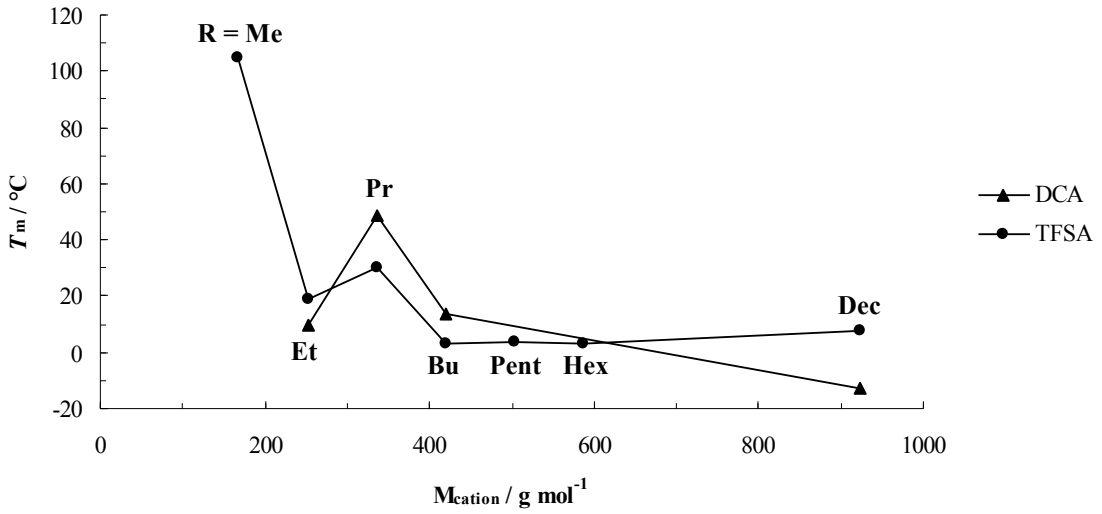


Figure 5.3 – Melting point verus molecular weight of $[C_3(NR_2)_3]^+$ cations with DCA and TFSA anions

The anion also plays a very important role. Furthermore, the anion and cation effects are not independent of each other. The general anion melting point trend is SCN < TFSA, DCA < BF_4 < NO_3, OTf < Cl, although there is only one data point for each of thiocyanate, nitrate and triflate. This anion trend is similar to other classes of cations.[6-9]

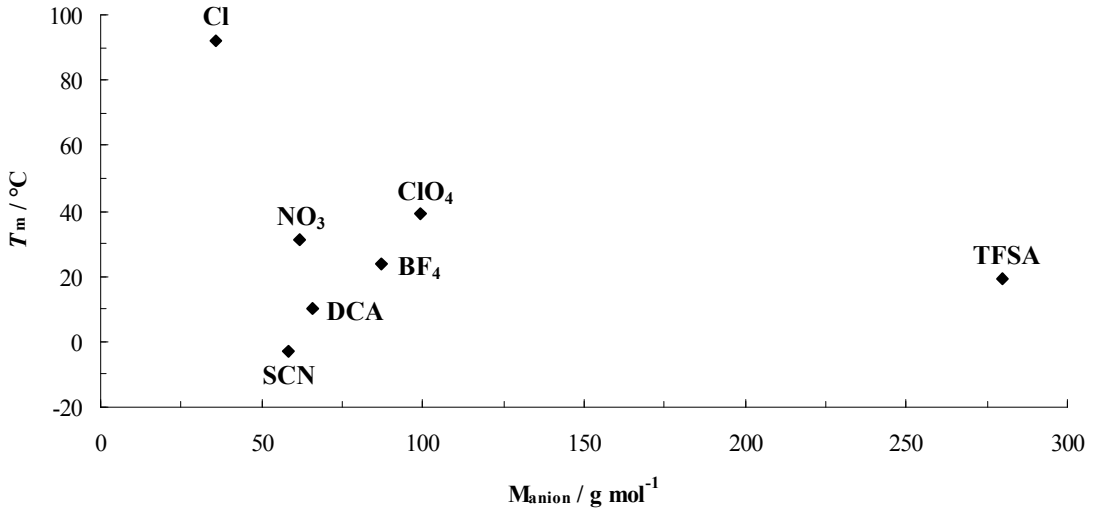


Figure 5.4 – Melting point versus molecular weight of the anion for $[C_3(NEt_2)_3]^+$ salts

Solid-solid transitions occur when a molecular motion is introduced, turning the solid crystal into a solid meso-phase that has long range order, but disorder in part of the compound.[10] The observed solid-solid transitions could be due to either the introduction of conformational flexibility or molecular rotation of either the anion or cation. In this work, only a few samples showed solid-solid transitions. Comparing ΔS for the solid-solid transition with ΔS_{fus}, it is seen that in all cases ΔS_{fus} is greater than ΔS, and in most cases ΔS_{fus} was relatively large, > 40 J mol^{-1} K^{-1}.[11,12] This means that the meso-phase phase is relatively ordered, suggesting it is likely a conformational rearrangement that has been introduced, rather than molecular rotation. It is also noted that many of the cations and anions used are not spherical, discouraging plastic crystal rotator phases. It should be noted that the error in the enthalpy measurements is relatively large, approximately 10%.

Only weak trends are observed in the glass transition temperatures (Figure 5.5). For the TFSA and DCA anion series, there is a slight increase in the glass transition temperature as the size of the cation increases. This is because viscosity is increasing, therefore, raising the temperature at which the viscosity reaches the glass threshold. The rough correlation between viscosity and glass transition temperature is seen in Figure 5.6. For the samples where both glass transitions and melting points are observed, it is seen that the glass transition is approximately 2/3 of the melting point, as has commonly been seen with other ionic liquids.[13]

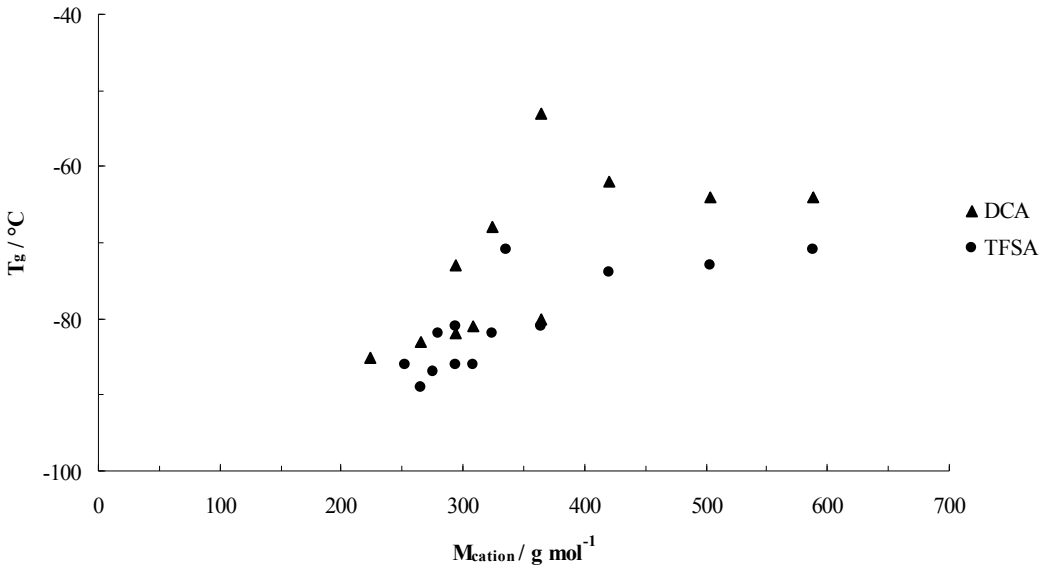


Figure 5.5 – Glass transition temperature versus molecular weight of cations, with TFSA and DCA anions

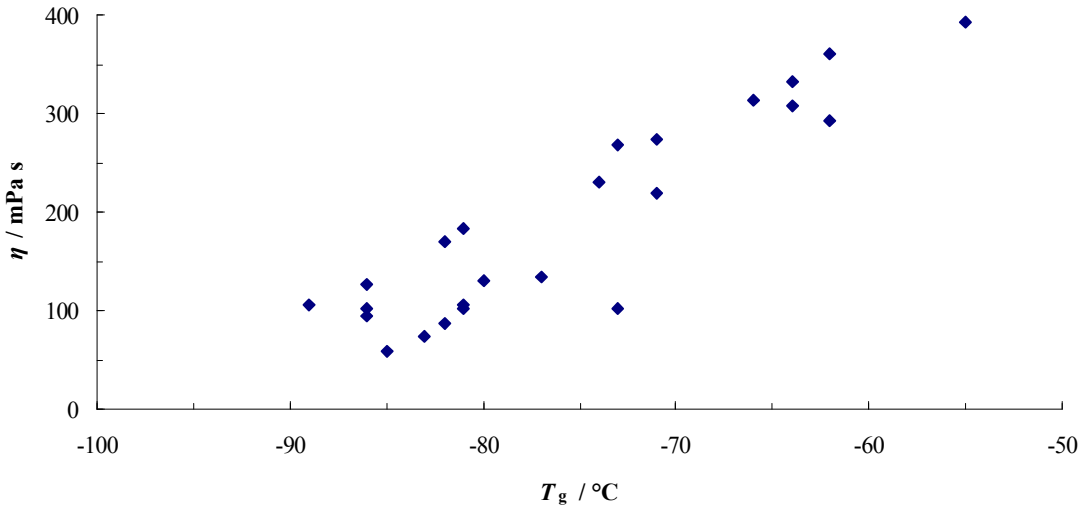


Figure 5.6 – Correlation between glass transition temperature and viscosity at 20 °C

5.3 Density

Densities of most ionic liquids are similar to molecular, organic liquids, although some incorporating heavy metal atoms are higher.

Densities of triaminocyclopropenium ionic liquids as a function of temperature are reported in Table 5-2. As would be expected, density decreases as temperature increases. The density of triaminocyclopropenium ionic liquids at 20 °C is shown in Figure 5.8. At 20 °C, the densities range from 0.890 for $[C_3(NDec_2)_3]$DCA up to 1.308 g mL^{-1} $[C_3(NEt_2)_2NMe_2]$TFSA. A major factor influencing density of the ionic liquids is the anion. The order from highest density to least is TFSA > ClO_4 > NO_3, BF_4 > SCN, DCA, Cl, which is approximately the order of the molecular weight of the anions.[14]

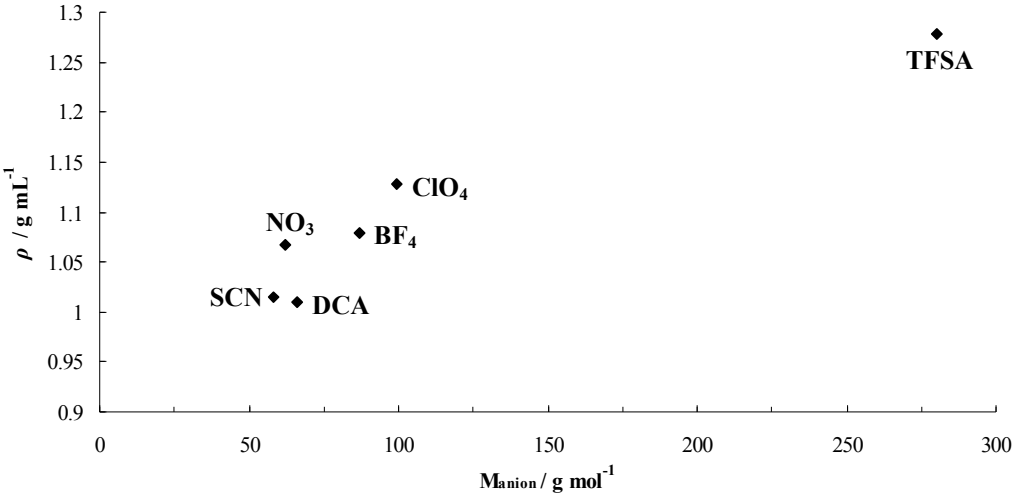


Figure 5.7 – Density at 20 °C versus molecular weight of the anion for $[C_3(NEt_2)_3]^+$ salts

It is seen that as the molecular weight of the cation increases the density decreases, which is expected due to the weaker nature of van der Waal forces compared to electrostatic forces (which are being diluted) and the lowering of the average atomic weight. Cation symmetry is not seen to play any role in determining the density, as D_{3h}, C_{3h}, C_{2v} and C_s symmetries all fall along the same curve (Figure 5.8). The only exceptions to this are $[C_3(NEt_2)_2NAllyl_2]$TFSA, $[C_3(NAllyl_2)_3]$TFSA, $[C_3(NAllyl_2)_3]$DCA and $[C_3(NEt_2)_2N(C_2H_4OH)_2]$TFSA. These cations all contain allyl or alcohol groups and presumably do not fall along the same curve as other alkyl chains because π-π interactions or hydrogen bond intermolecular forces are also occurring.

Table 5-2 – Density of triaminocyclopropenium ionic liquids

		ρ / g mL^{-1}							
		20 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C
D_{3h}	$[C_3(NEt_2)_3]BF_4$	1.079	1.072	1.066	1.059	1.052	1.045	1.038	1.032
	$[C_3(NEt_2)_3]ClO4$	1.128	1.121	1.114	1.108	1.101	1.095	1.088	1.082
	$[C_3(NEt_2)_3]DCA$	1.010	1.004	0.998	0.992	0.985	0.979	0.973	0.967
	$[C_3(NEt_2)_3]NO_3$	1.066	1.060	1.054	1.048	1.042	1.036	1.030	1.024
	$[C_3(NEt_2)_3]SCN$	1.015	1.008	1.003	0.997	0.991	0.985	0.980	0.974
	$[C_3(NEt_2)_3]TFSA$	1.277	1.269	1.260	1.251	1.243	1.234	1.226	1.217
	$[C_3(NAllyl_2)_3]DCA$	1.027	1.021	1.015	1.008	1.002	0.996	0.989	0.983
	$[C_3(NAllyl_2)_3]TFSA$	1.250	1.242	1.233	1.225	1.216	1.208	1.199	1.191
	$[C_3(NPr_2)_3]DCA$	0.975	0.969	0.963	0.957	0.951	0.945	0.939	0.933
	$[C_3(NPr_2)_3]NO_3$	1.014		1.002	0.995	0.989	0.983	0.977	0.971
	$[C_3(NPr_2)_3]TFSA$	1.196	1.188	1.179	1.171	1.163	1.155	1.147	1.139
	$[C_3(NBu_2)_3]BF_4$	0.993	0.986	0.980	0.973	0.967	0.960	0.954	0.947
	$[C_3(NBu_2)_3]Cl$	0.939	0.933	0.927	0.921	0.915	0.909	0.903	0.898
	$[C_3(NBu_2)_3]DCA$	0.944	0.938	0.932	0.926	0.920	0.914	0.908	0.902
	$[C_3(NBu_2)_3]NO_3$	0.973	0.967	0.960	0.954	0.948	0.942	0.936	0.930
	$[C_3(NBu_2)_3]OTf$			1.029	1.023	1.016	1.009	1.002	0.995
	$[C_3(NBu_2)_3]TFSA$	1.134	1.127	1.119	1.111	1.103	1.095	1.088	1.080
	$[C_3(NPent_2)_3]DCA$	0.927	0.921	0.915	0.909	0.903	0.897	0.891	0.885
	$[C_3(NPent_2)_3]TFSA$	1.086	1.079	1.072	1.064	1.057	1.050	1.043	1.036
	$[C_3(NHex_2)_3]DCA$	0.915	0.909	0.903	0.897	0.891	0.885	0.879	0.873
	$[C_3(NHex_2)_3]TFSA$	1.059	1.051	1.044	1.037	1.030	1.022	1.015	1.008
	$[C_3(NHex_2)_3]DBP$	0.921	0.915	0.908	0.902	0.895	0.888	0.882	0.875
	$[C_3(NDec_2)_3]DCA$	0.890	0.884	0.878	0.872	0.866	0.860	0.854	0.849
	$[C_3(NDec_2)_3]TFSA$	0.991	0.984	0.977	0.970	0.964	0.957	0.950	0.943
C_{3h}	$[C_3(NBuMe)_3]DCA$	0.983	0.977	0.970	0.964	0.958	0.952	0.947	0.941
	$[C_3(NBuMe)_3]TFSA$	1.224	1.216	1.207	1.199	1.191	1.183	1.174	1.166

		ρ / g mL^{-1}							
		20 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C
C_{2v}	$[C_3(NEt_2)_2NMe_2]DCA$	1.023	1.017	1.010	1.004	0.998	0.992	0.986	0.980
	$[C_3(NEt_2)_2NMe_2]TFSA$	1.308	1.299	1.291	1.282	1.273	1.264	1.256	1.247
	$[C_3(NEt_2)_2NAllyl_2]TFSA$	1.270	1.261	1.252	1.244	1.235	1.226	1.218	1.209
	$[C_3(NEt_2)_2NBu_2]DCA$	0.980	0.974	0.968	0.962	0.955	0.949	0.943	0.937
	$[C_3(NEt_2)_2NBu_2]TFSA$	1.216	1.208	1.200	1.191	1.183	1.175	1.167	1.159
	$[C_3(NEt_2)_2NHex_2]DCA$	0.958	0.952	0.946	0.939	0.933	0.927	0.922	0.916
	$[C_3(NEt_2)_2NHex_2]TFSA$	1.171	1.163	1.155	1.147	1.139	1.131	1.123	1.115
	$[C_3(NEt_2)_2N(C_2H_4OH)_2]TFSA$	1.256	1.247	1.239	1.230	1.222	1.214	1.206	1.198
C_s	$[C_3(NEt_2)_2NBuMe]DCA$	0.999	0.993	0.987	0.981	0.975	0.969	0.963	0.957
	$[C_3(NEt_2)_2NBuMe]TFSA$	1.260	1.251	1.243	1.235	1.226	1.218	1.209	1.201
	$[C_3(NEt_2)_2NHexMe]DCA$	0.984	0.978	0.972	0.966	0.960	0.954	0.948	0.942
	$[C_3(NEt_2)_2NHexMe]TFSA$	1.228	1.220	1.211	1.203	1.195	1.187	1.178	1.170

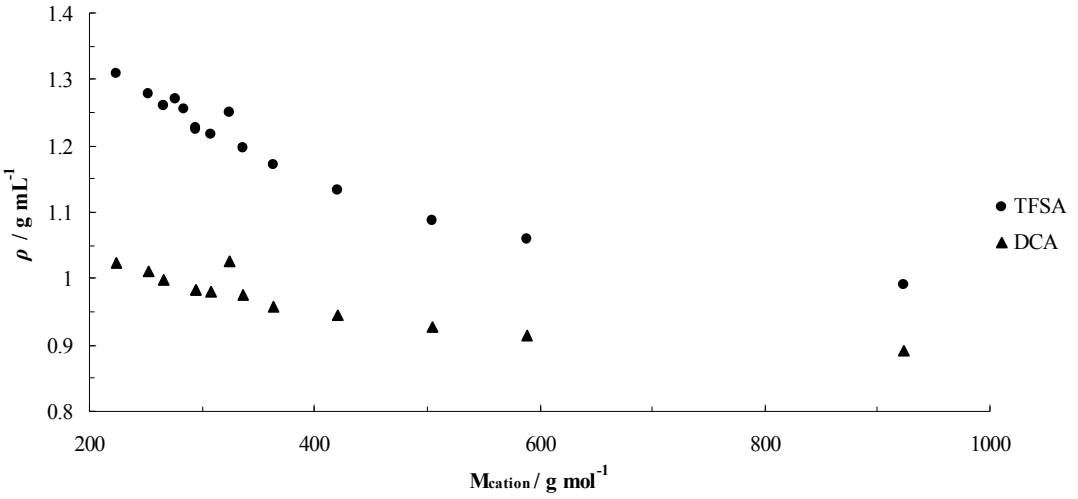


Figure 5.8– Density at 20 °C versus cation molecular weight

Compared to other classes of ionic liquids,[14-17] triaminocyclopropenium ionic liquid densities are slightly lower, however, this is not due to the nature of the triaminocyclopropenium cation directly, and is instead due to their large molecular weight. For example, $[C_{10}MIM]TFSA$ (223.4 g mol^{-1})has a density of 1.260 g mL^{-1} at 22 °C,[18] similar to the density of $[C_3(NEt_2)_2NMe_2]TFSA$ (224.4 g mol^{-1}) at 20 °C, 1.308 g mL^{-1}.

Due to the relatively large size of triaminocyclopropenium cations, their molar volumes are large, and inversely their molar concentration is low. At 20 °C, the molar volumes range from 284 mL mol^{-1} for $[C_3(NEt_2)_2NMe_2]DCA$ to 1215 mL mol^{-1} for $[C_3(NDec_2)_3]TFSA$. Other smaller ionic liquids have lower molar volumes, for example, $[C_2MIM]DCA$ has a molar volume of 161 at 25 °C.[19]

Density is highly linearly dependent on temperature. As an example of this, the density of $[C_3(NEt_2)_3]TFSA$ is shown in Figure 5.9. The linear temperature dependence of density was fitted for all samples (Table 5-3).

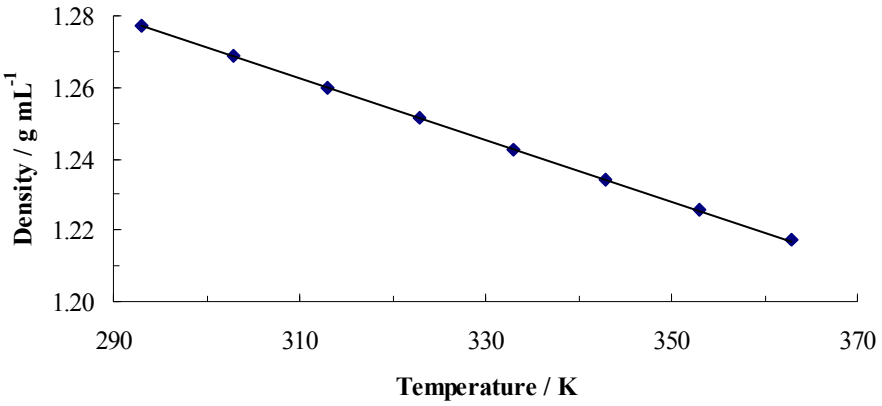


Figure 5.9 – Temperature dependence of density and a linear fit of $[C_3(NEt_2)_3]TFSA$

Table 5-3 – Fitting parameters for temperature dependence of density, $\rho = a - bT$

		$-b$ x10^{-4} g mL^{-1} K^{-1}	a g mL^{-1}	δ x10^{-4}
D_{3h}	$[C_3(NEt_2)_3]BF_4$	6.8077	1.2787	0.8
	$[C_3(NEt_2)_3]ClO4$	6.5124	1.3182	1.2
	$[C_3(NEt_2)_3]DCA$	6.1229	1.1894	0.8
	$[C_3(NEt_2)_3]NO_3$	6.0817	1.2445	0.8
	$[C_3(NEt_2)_3]SCN$	5.7657	1.1831	1.9
	$[C_3(NEt_2)_3]TFSA$	8.5758	1.5284	1.0
	$[C_3(NAllyl_2)_3]DCA$	6.3224	1.2124	0.9
	$[C_3(NAllyl_2)_3]TFSA$	8.4878	1.4988	1.5
	$[C_3(NPr_2)_3]DCA$	5.9893	1.1504	0.8
	$[C_3(NPr_2)_3]NO_3$	9.7105	1.3186	1.2
	$[C_3(NPr_2)_3]TFSA$	8.1255	1.4337	1.1
	$[C_3(NBu_2)_3]BF_4$	6.4977	1.1832	1.1
	$[C_3(NBu_2)_3]Cl$	5.9070	1.1119	2.2
	$[C_3(NBu_2)_3]DCA$	5.9528	1.1183	0.7
	$[C_3(NBu_2)_3]NO_3$	6.0369	1.1494	1.1
	$[C_3(NBu_2)_3]OTf$	6.7982	1.2422	0.3
	$[C_3(NBu_2)_3]TFSA$	7.7552	1.3615	0.6
	$[C_3(NPent_2)_3]DCA$	5.9728	1.1021	0.9
	$[C_3(NPent_2)_3]TFSA$	7.1614	1.2959	1.7
	$[C_3(NHex_2)_3]DCA$	5.9623	1.0896	0.6
	$[C_3(NHex_2)_3]TFSA$	7.2629	1.2715	0.6
	$[C_3(NHex_2)_3]DBP$	6.5369	1.1127	0.5
	$[C_3(NDec_2)_3]DCA$	5.9575	1.0648	1.1
	$[C_3(NDec_2)_3]TFSA$	6.8118	1.1905	1.1

		$-b$ x10^{-4} / g mL^{-1} K^{-1}	a / g mL^{-1}	δ x10^{-4}
C_{3h}	$[C_3(NBuMe)_3]$DCA	5.9801	1.1577	0.8
	$[C_3(NBuMe)_3]$TFSA	8.2212	1.4646	1.1
C_{2v}	$[C_3(NEt_2)_2NMe_2]$DCA	6.1100	1.2016	1.1
	$[C_3(NEt_2)_2NMe_2]$TFSA	8.7094	1.5633	1.1
	$[C_3(NEt_2)_2NAllyl_2]$TFSA	8.6818	1.5241	1.2
	$[C_3(NEt_2)_2NBu_2]$DCA	6.1445	1.1160	0.5
	$[C_3(NEt_2)_2NBu_2]$TFSA	8.1933	1.4562	0.8
	$[C_3(NEt_2)_2NHex_2]$DCA	6.0060	1.1335	0.6
	$[C_3(NEt_2)_2NHex_2]$TFSA	7.8806	1.4014	0.5
	$[C_3(NEt_2)_2N(C_2H_4OH)_2]$TFSA	8.2765	1.4979	2.4
C_s	$[C_3(NEt_2)_2NBuMe]$DCA	6.0245	1.1759	0.8
	$[C_3(NEt_2)_2NBuMe]$TFSA	8.4032	1.5061	0.9
	$[C_3(NEt_2)_2NHexMe]$DCA	5.9286	1.1571	0.8
	$[C_3(NEt_2)_2NHexMe]$TFSA	8.2042	1.4681	1.0

5.4 Viscosity

Viscosity is an important property for liquids, affecting handling and many properties such as mixing, diffusion and conductivity. The viscosities of ionic liquids are much higher than that of common molecular solvents. However, this is usually not prohibitive to their use, especially at elevated temperatures, due to a rapid decrease in viscosity as temperature increases.

This work has measured the dynamic viscosity for a range of triaminocyclopropenium ionic liquids over a temperature range of usually 20 to 90 °C, depending on the melting point. Viscosity was measured on a Brookfield cone and plate viscometer. This uses a small sample size (approximately 0.8 mL), measures viscosity between 1 and 1000 mPa s, has temperature control through a circulating water jacket and the sample is blanketed with dry nitrogen gas to avoid absorption of atmospheric moisture.

The cone and plate viscometer is also capable of measuring the viscosity of non-Newtonian fluids, as the cone is turned with a known shear rate and measures the shear stress. In this work, non-Newtonian behaviour was looked for by varying the shear rate (3 points, increasing by a factor of two at each one) while holding the temperature constant.

No substantial variation of the viscosity was observed within the shear rate range and the accuracy limits of the viscometer (±1%).

The dynamic viscosities (η) are recorded in Table 5-4, with the viscosity at 20 °C plotted in Figure 5.11. If kinematic viscosity (υ) is required, this can be obtained using the density (ρ), Equation 3.

$$\upsilon = \frac{\eta}{\rho}$$

Equation 3

For all triaminocyclopropenium ionic liquids measured there was a large drop-off in viscosity as the temperature increased (Figure 5.10). For example $[C_3(NDec_2)_3]DCA$ decreases from 554 at 20 °C to 20.8 mPa s at 90 °C. During the course of the experiments, no sudden changes in viscosity were observed, showing that no phase changes occur over the temperature range studied. In the cases of $[C_3(NEt_2)_3]ClO_4$, $[C_3(NPr_2)_3]DCA$, $[C_3(NBu_2)_3]BF_4$ and $[C_3(NBu_2)_3]OTf$, viscosities could only be recorded above the melting point. In the cases of $[C_3(NPr_2)_3]NO_3$, $[C_3(NBu_2)_3]Cl$ and $[C_3(NBu_2)_3]NO_3$ viscosity could only be recorded when the temperature was increased enough to bring viscosity into the viscometer's range.

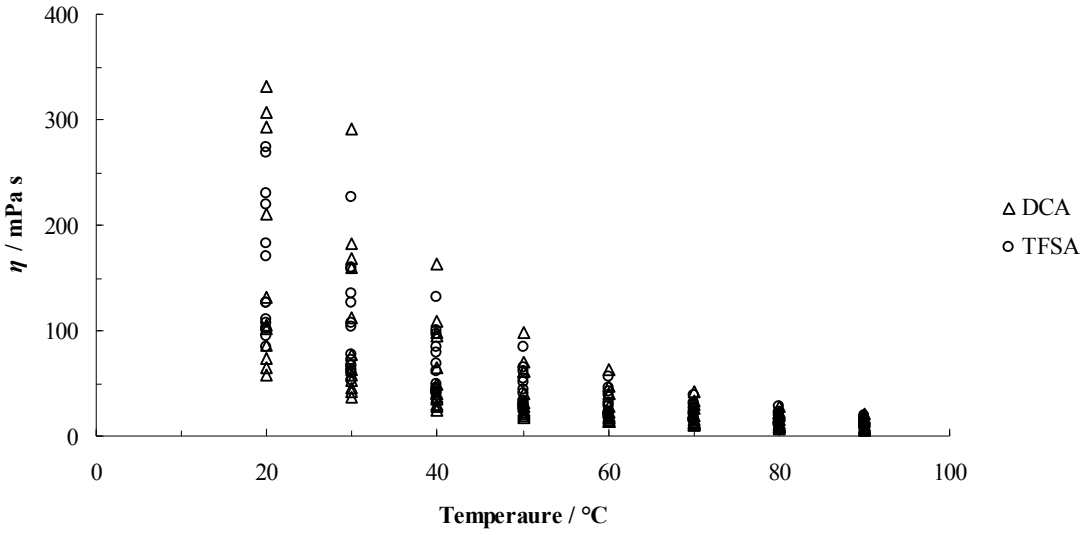


Figure 5.10 – Dynamic viscosity versus temperature for TFSA and DCA triaminocyclopropenium ionic liquids

As expected, longer alkyl chains are clearly shown to increase viscosity. This occurs in all symmetry series, Figure 5.11. In the D_{3h} series at 20 °C, the lowest viscosity for each anion is with the $[C_3(NEt_2)_3]^+$ cation, with the lowest being $[C_3(NEt_2)_3]$DCA at 64.2 mPa. As the alkyl chains are lengthened, molecules find it harder to move past each other, thus increasing the viscosity. The highest viscosities are with the longest alkyl chain, $[C_3(NDec_2)_3]$DCA at 554 mPa s and $[C_3(NDec_2)_3]$TFSA 408 mPa s, which is quite low considering the size of this cation. In the C_{2v} series, the lowest viscosity is $[C_3(NEt_2)_2NMe_2]$DCA at 58.4 mPa s, which is also the lowest viscosity recorded in this work. The only exception, at 20 °C, to longer chains causing high viscosity involved the C_s $[C_3(NEt_2)_2NBuMe]$TFSA, at 106 mPa s, and $[C_3(NEt_2)_2NHexMe]$TFSA, slightly less viscous at 102 mPa s. This may be due to $[C_3(NEt_2)_2NHexMe]^+$'s lack of symmetry being more prominent, without dramatically hindering the movement of nearby molecules.

Table 5-4 – Summary of Viscosity measurements

			η / mPa s							
		M_{cation} g mol^{-1}	20 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C
D_{3h}	$[C_3(NEt_2)_3]BF_4$	252	206	115	69.3	43.7	29.4	21.0	15.5	11.8
	$[C_3(NEt_2)_3]ClO4$	252	–	–	136	81.7	52.5	35.8	25.3	18.5
	$[C_3(NEt_2)_3]DCA$	252	64.2	41.9	28.3	19.9	14.6	11.4	8.9	7.1
	$[C_3(NEt_2)_3]NO_3$	252	313	169	98.5	61.3	41.0	28.8	20.6	–
	$[C_3(NEt_2)_3]SCN$	252	134	79.1	49.7	33.5	23.5	17.2	12.9	10.0
	$[C_3(NEt_2)_3]TFSA$	252	94.7	60.5	40.0	27.5	19.6	15.0	11.5	9.0
	$[C_3(NPr_2)_3]DCA$	336	–	–	–	–	14.6	10.2	7.5	5.7
	$[C_3(NPr_2)_3]NO_3$	336	–	–	490	252	141	86.2	55.0	36.6
	$[C_3(NPr_2)_3]TFSA$	336	220	127	78.3	50.1	32.3	22.6	16.6	12.6
	$[C_3(NAllyl_2)_3]DCA$	324	211	113	65.3	41.1	27.2	19.3	15.2	10.7
	$[C_3(NAllyl_2)_3]TFSA$	324	126	72.6	45.5	30.8	21.1	15.3	11.4	8.6
	$[C_3(NBu_2)_3]BF_4$	420	–	546	276	153	89.9	56.8	37.5	26.4
	$[C_3(NBu_2)_3]Cl$	420	–	–	–	1446	674	347	193	120
	$[C_3(NBu_2)_3]DCA$	420	293	160	95.0	60.6	41.0	29.0	21.5	16.4
	$[C_3(NBu_2)_3]NO_3$	420	–	–	500	264	152	90.3	56.8	38.5
	$[C_3(NBu_2)_3]OTf$	420	–	–	–	39.2	24.9	16.7	11.6	7.3
	$[C_3(NBu_2)_3]TFSA$	420	230	134	83.6	55.2	38.3	26.9	19.2	13.9
	$[C_3(NPent_2)_3]DCA$	504	308	168	97.9	60.9	40.0	27.0	19.8	14.4
	$[C_3(NPent_2)_3]TFSA$	504	269	158	97.1	62.1	41.9	29.3	21.3	16.1
	$[C_3(NHex_2)_3]DCA$	588	332	183	109	69.4	46.9	32.9	23.5	17.8
	$[C_3(NHex_2)_3]TFSA$	588	273	159	99.6	65.3	44.9	32.4	23.6	17.8
	$[C_3(NHex_2)_3]DBP$	588	227	126	73.0	45.6	30.2	21.5	15.2	11.3
	$[C_3(NDec_2)_3]DCA$	924	554	291	163	97.5	62.3	41.6	28.9	20.8
	$[C_3(NDec_2)_3]TFSA$	924	408	227	132	84.6	56.0	38.4	27.2	20.0

			η / mPa s							
		M_{cation} g mol^{-1}	20 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C
C_{3h}	$[C_3(NBuMe)_3]BF_4$	294	360	184	102	60.8	39.9	28.0	20.5	14.8
	$[C_3(NBuMe)_3]DCA$	294	101	58.6	36.6	24.1	16.9	12.4	9.5	7.3
	$[C_3(NBuMe)_3]NO_3$	294	392	199	108	64.4	40.8	27.0	19.0	14.0
	$[C_3(NBuMe)_3]TFSA$	294	101	61.9	39.8	26.8	19.0	13.9	10.6	8.2
C_{2v}	$[C_3(NEt_2)_2NMe_2]DCA$	224	58.4	37.1	25.4	17.9	13.2	10	7.94	6.41
	$[C_3(NEt_2)_2NMe_2]TFSA$	224	83.6	52.4	35.2	24.7	17.9	13.4	10.3	8.2
	$[C_3(NEt_2)_2NAllyl_2]TFSA$	276	111	67.4	43.7	29.6	20.9	15.3	11.7	9.0
	$[C_3(NEt_2)_2NBu_2]DCA$	308	105	63.3	40.8	27.4	19.4	14.2	11.0	8.6
	$[C_3(NEt_2)_2NBu_2]TFSA$	308	126	76.4	49.9	32.7	23.1	17.2	13.0	9.9
	$[C_3(NEt_2)_2NHex_2]DCA$	364	131	76.8	48.4	32.0	22.2	16.0	12.0	9.3
	$[C_3(NEt_2)_2NHex_2]TFSA$	364	182	108	67.8	44.2	30.2	21.7	15.8	12.0
	$[C_3(NEt_2)_2N(C_2H_4OH)_2]TFSA$	348	–	–	249	143	89.0	58.5	40.1	28.7
C_s	$[C_3(NEt_2)_2NBuMe]DCA$	266	73.7	45.8	30.2	20.8	15.3	11.5	8.9	7.1
	$[C_3(NEt_2)_2NBuMe]TFSA$	266	106	66.4	43.3	29.7	21.1	15.5	11.9	9.1
	$[C_3(NEt_2)_2NHexH]TFSA$	280	171	103	61.3	40.8	27.9	20.4	15.2	11.4
	$[C_3(NEt_2)_2NHexMe]DCA$	294	86.2	52.8	34.4	23.4	17.0	12.7	9.8	7.7
	$[C_3(NEt_2)_2NHexMe]TFSA$	294	102	62.8	41.4	28.3	20.3	15.2	11.6	9.1

It is interesting to compare triaminocyclopropenium ionic liquid viscosities with those of other cation classes. At 60 °C, a kinematic viscosity of 54.3 cSt was observed in $[C_{18}MIM]TFSA$[20] which is very similar to $[C_3(NDec_2)_3]TFSA$ at 58.1 cSt, despite the much larger size of the triaminocyclopropenium cation (925.7 g mol^{-1} vs 347.6 g mol^{-1}). Of course, a single alkyl chain on the imidazolium cation will give a lower viscosity than six alkyl chains of the same length on a triaminocyclopropenium cation. For example, $[C_{10}MIM]TFSA$ (223.4 g mol^{-1}) has a viscosity of 124 mPa s at 20 °C,[18] much lower than $[C_3(NDec_2)_3]TFSA$. However the similarily sized $[C_3(NEt_2)_2NMe_2]TFSA$ (224.4 g mol^{-1}) has a lower viscosity at 83.6 mPa s. This is probably due to triaminocyclopropenium having a disperse charge and fewer intermolecular interactions such as weak hydrogen bond donors on the imidazolium cation. The electron rich nature of the triaminocyclopropenium cation may also be having an effect. When comparing to ammonium,[1,21,22] phosphonium[23] or guanidinium[21,24] cations, many different arrangements of the alkyl chains are possible for the same-sized cation, which makes many different comparisons possible. For comparable sized cations, triaminocyclopropenium ionic liquids have lower viscosity than other classes of ionic liquids, however, due to smaller cations being possible with the other classes than the triaminocyclopropenium cations investigated here, the other classes reach lower viscosities.

The symmetry of the cation does not have a large effect on the viscosity of the triaminocyclopropenium ionic liquids measured, rather it is mainly the size of the cation that determines the viscosity. Increased molecular mass of the cation increased the viscosity markedly, from less than 100 mPa s, for small cations to 554 mPa s for $[C_3(NDec_2)_3]DCA$. Symmetry has a small effect in the relationship between the anion and viscosity. The anion trend for cations larger than 400 g mol^{-1} is TFSA < DCA < SCN < BF_4 < NO_3 < Cl, however, in the cases of small cations, such as $[C_3(NEt_2)_3]^+$, the order of TFSA and DCA is reversed. This is perhaps this is due to the larger anion TFSA being less affected by longer alkyl chains tangling together.

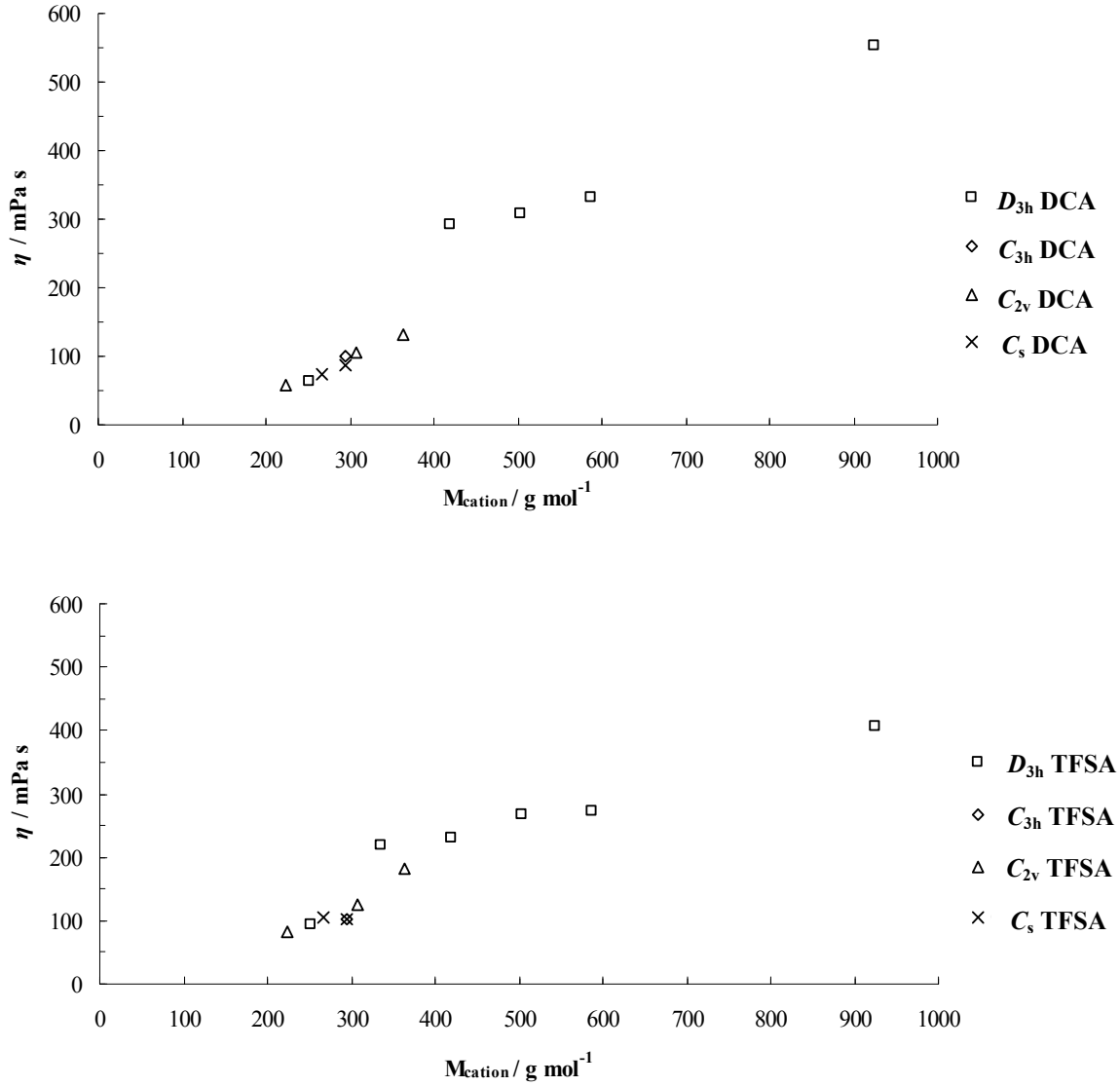


Figure 5.11 – Dynamic viscosity at 20 °C versus molecular weight of the cation, for DCA (top) and TFSA (bottom) salts with alkyl substituents

A number of intermolecular forces are also observed to play a role in viscosity. Hydrogen bonds will increase viscosity, for example, at 20 °C, $[C_3(NEt_2)_2NHexH]TFSA$ has a viscosity of 171 mPa s, compared to $[C_3(NEt_2)_2NHexMe]TFSA$ which has a viscosity of 102 mPa s. $[C_3(NEt_2)_2N(C_2H_4OH)_2]TFSA$ has a viscosity of 249 mPa s, at 40 °C. Also, $[C_3(N(C_2H_4OH)_2)_3]^+$ salts were extremely viscous, so much so it could not be handled as a liquid.

Unsaturated alkyl chains also affected viscosities. For example at 20 °C, $[C_3(NAllyl_2)_3]$TFSA has a viscosity of 126 mPa s, compared to 220 mPa s for $[C_3(NPr_2)_3]$TFSA. It is interesting to note that $[C_3(NAllyl_2)_3]$DCA has a viscosity of 211 mPa s, much higher viscosity than the TFSA salt, presumably due to π-π intermolecular forces, between DCA and the allyl groups.

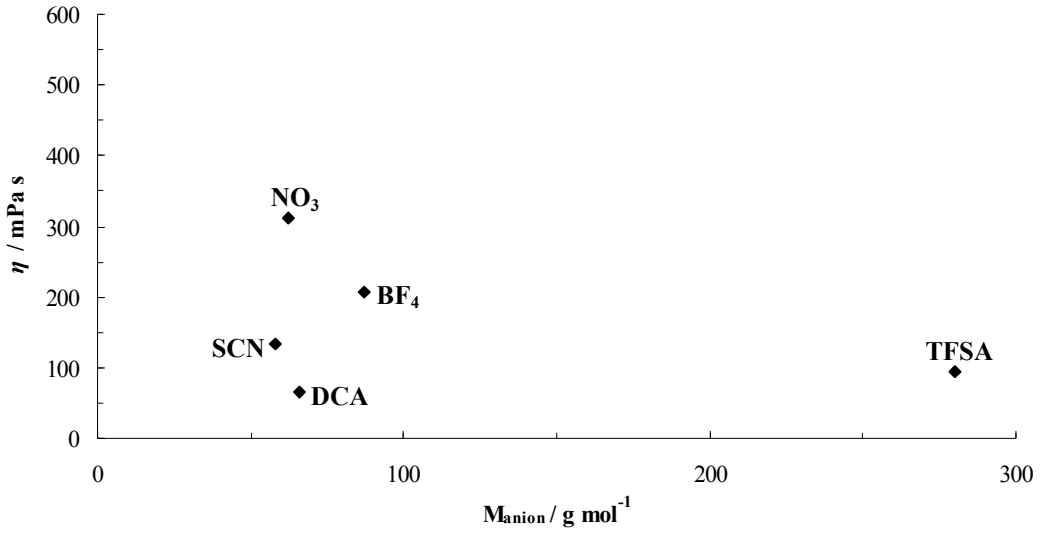


Figure 5.12 – Viscosity at 20 °C versus molecular weight of the anion for $[C_3(NEt_2)_3]^+$ salts

When the viscosity of D_{3h} cations with straight, saturated alkyl chains with either TFSA (Figure 5.13a) or DCA (Figure 5.13b) anions is plotted against chain length, an alternating sequence of high and low viscosity is seen, similar to the alternating sequence seen in the melting points of D_{3h} straight, saturated alkyl chain TFSA salts. In the TFSA series even numbered alkyl chain lengths seem to result in relatively lower viscosity. This is consistent with the alternating melting point effect, as compounds that do not pack together well will have lower melting points and lower viscosities. The alternating effect is strongest at 20 °C, decreasing until it is not obvious above 50 °C. In the DCA series, the $[C_3(NPr_2)_3]^+$ salt was unfortunately solid below 60 °C. Unlike the TFSA series in the DCA series the even numbered alkyl chains have relatively higher viscosities. Also the alternating effect seems to be increasing with temperature.

It is speculated that the alternating effect observed may be due to certain combinations of anions and alkyl chain lengths not fitting as well together in an alternating fashion, due to size or shape, as other combinations. This may increase the probability of creating a hole or probability of creating a larger hole, both of which would decrease viscosity according to hole theory.[25] The anion dependence of the alternating effect could be explained due to the TFSA and DCA having different size and shape, so the combination with even or odd chain lengths that results in lower viscosity is not necessarily the same with each anion. The temperature dependence of the alternating effect could be due to the temperature affecting the effective size of the molecules.

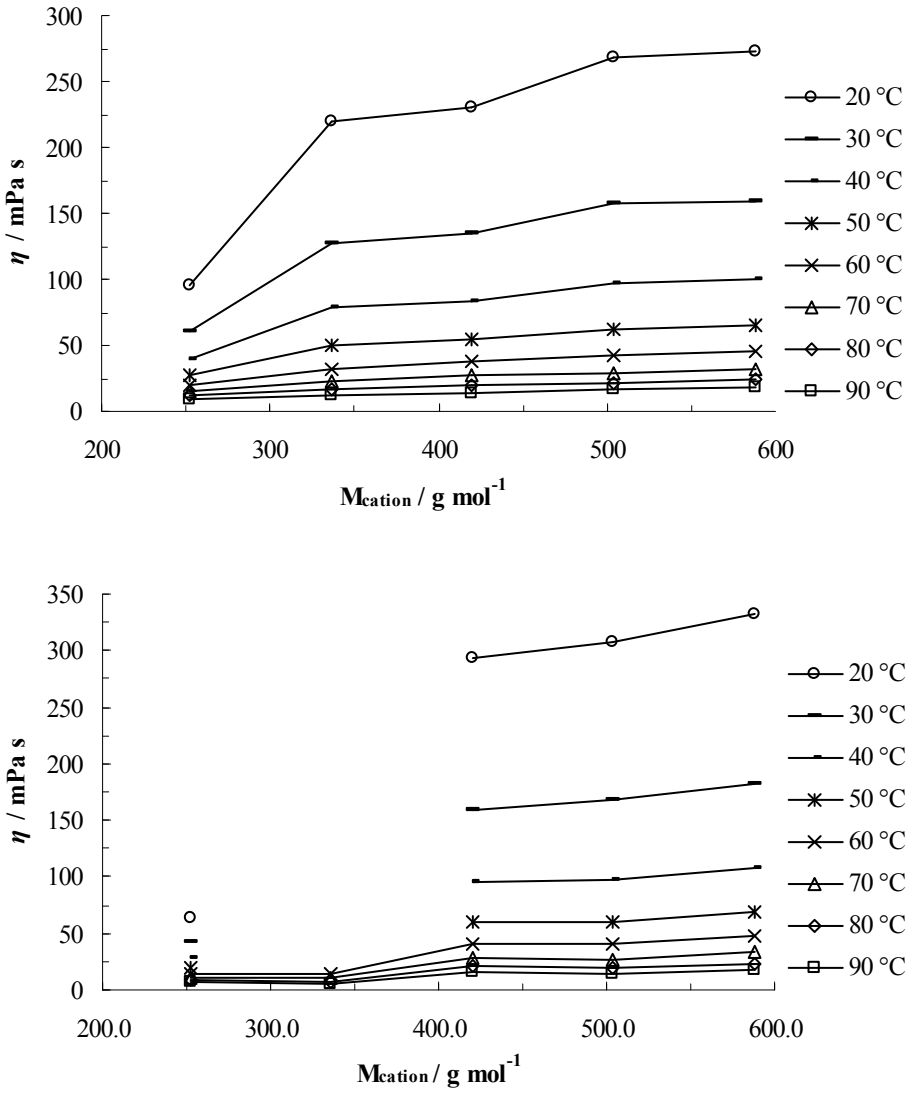


Figure 5.13 – D_{3h} C_n cations, n = 2-6 a) Top TFSA series. b) Bottom DCA series

The viscosity data were fitted to the Vogel-Fulcher-Tammann (VFT) and Arrhenius empirical equations, Equation 4 and Equation 5, respectively, to model the temperature dependence of viscosity. The parameters were found by least squares fitting, Table 5-5. The standard deviation (σ) of the data from the fitted model is also given, and from this it is seen that the VFT equation is more accurate than the fitting with the Arrhenius equation.

In the VFT equation, η_0, B and T_0 are constants. B and T_0 can be related to the parameter D, $D = B/T_0$, which is also sometimes expressed as $F = T_0/B$. D (and F) quantify the deviation from Arrhenius behaviour, which is known as the fragility of the liquid. A D value of less than 10 means the liquid is fragile, whereas for a strong liquid, D is nearer to 100. Thus, it is seen that nearly all the triaminocyclopropenium ionic liquids reported here are fragile. T_0 can be described as the ideal glass transition temperature, the temperature at which point the molecules are in a state of closest random packed with no conformational entropy[17] (i.e. not moving). The difference between the Arrhenius equation and the VFT equation is that the Arrhenius equation has the ideal glass transition state occurring at 0 K whereas for the VFT equation this occurs at T_0.[26] It is always seen that $T_g > T_0$, because the sample freezes before thermodynamic equilibrium for the ideal glass state is reached. The difference between T_g and T_0 is related to D;[27] when D is small, T_0 tends to be close to T_g.

Viscosity data for $[C_3(NPr_2)_3]$DCA, $[C_3(NBu_2)_3]$OTf and $[C_3(NBu_2)_3]$TFSA salts have not produced sensible VTF parameters compared to the other salts, despite having a low standard deviation, probably due to a limited number of datapoints. Low T_0 and high B parameters, counteracted by a low η_0, produced high D values. Later, in the Tg/T scaled Arrhenius plot (Figure 5.14), it will be seen that these cases do not stand out as being more or less fragile.

Within the cation series, there are no strong trends of the VFT parameters identified for varying cations size or symmetry, however, there is a weak trend of a higher D value as molecular weight increases. Within the anions series, it is seen that B, and consequently

D values, are higher for the TFSA salts than the corresponding DCA salts, i.e. less fragile.

The Arrhenius equation was also fitted to the viscosity data. As already mentioned this has a substantially higher standard deviation than the VFT equation, although it can still be used to model the viscosity within the 20 to 90 °C temperature range used. The activation energies, E_a, for viscosity were determined to be between 28 and 61 kJ mol^{-1}, increasing as viscosity increases.

$$\eta = \eta_0 \exp\left(\frac{B}{T - T_0}\right) = \eta_0 \exp\left(\frac{DT_0}{T - T_0}\right)$$

Equation 4 – Vogel-Fulcher-Tammann (VFT) equation

$$\eta = A \exp\left(\frac{E_a}{RT}\right)$$

Equation 5 – Arrhenius equation

Table 5-5 – Fitting parameters

		η_0	B	T_0	D	δ	A x10^3	E_a	δ
		mPa s	K	K		mPa s	mPa s	kJ mol^{-1}	mPa s
D_{3h}	$[C_3(NEt_2)_3]BF_4$	0.078	966	171	5.7	0.6	0.069	36	7.6
	$[C_3(NEt_2)_3]ClO4$	0.076	1035	175	5.9	0.2	0.070	38	3.0
	$[C_3(NEt_2)_3]DCA$	0.088	920	154	6.0	0.2	0.673	28	1.5
	$[C_3(NEt_2)_3]NO_3$	0.076	1030	169	6.1	0.4	0.035	39	11.0
	$[C_3(NEt_2)_3]SCN$	0.076	985	161	6.1	0.1	0.190	33	4.3
	$[C_3(NEt_2)_3]TFSA$	0.067	1057	148	7.2	0.4	0.458	30	2.1
	$[C_3(NPr_2)_3]DCA$	0.004	1919	100	19.1	0.1	0.166	31	0.1
	$[C_3(NPr_2)_3]NO_3$	0.034	1291	178	7.2	0.6	0.0033	49	12.0
	$[C_3(NPr_2)_3]TFSA$	0.021	1438	138	10.4	1.2	0.068	36	4.9
	$[C_3(NAllyl_2)_3]DCA$	0.117	806	186	4.3	0.7	0.046	37	9.9
	$[C_3(NAllyl_2)_3]TFSA$	0.043	1111	154	7.2	0.5	0.122	34	4.0
	$[C_3(NBu_2)_3]BF_4$	0.034	1269	172	7.4	0.8	0.0055	46	18.9
	$[C_3(NBu_2)_3]Cl$	0.084	1134	207	5.5	3.7	0.00020	61	40.2
	$[C_3(NBu_2)_3]DCA$	0.140	883	178	5.0	0.2	0.091	36	12.4
	$[C_3(NBu_2)_3]NO_3$	0.012	1675	156	10.7	1.0	0.0038	49	10.1
	$[C_3(NBu_2)_3]OTf$	0.00012	3417	54	62.8	0.4	0.012	40	0.4
	$[C_3(NBu_2)_3]TFSA$	0.0082	1919	106	18.2	1.3	0.112	35	6.9

		η_0 mPa s	B K	T_0 K	D	δ mPa s	A x10^3 mPa s	E_a kJ mol^{-1}	δ mPa s
D_{3h}	$[C_3(NPent_2)_3]DCA$	0.032	1276	154	8.3	0.5	0.038	39	10.0
	$[C_3(NPent_2)_3]TFSA$	0.025	1481	134	11.1	1.0	0.111	36	5.8
	$[C_3(NHex_2)_3]DCA$	0.070	1121	161	7.0	0.5	0.084	37	12.0
	$[C_3(NHex_2)_3]TFSA$	0.051	1291	143	9.1	0.4	0.196	34	7.4
	$[C_3(NHex_2)_3]DBP$	0.037	1167	160	7.3	0.8	0.039	38	7.7
	$[C_3(NDec_2)_3]DCA$	0.026	1419	151	9.4	1.3	0.021	41	18.2
	$[C_3(NDec_2)_3]TFSA$	0.029	1452	141	10.3	0.8	0.065	38	11.7
C_{3h}	$[C_3(NBuMe)_3]BF_4$	0.122	846	187	4.5	1.6	0.024	40	18.2
	$[C_3(NBuMe)_3]DCA$	0.093	815	177	4.6	0.2	0.121	33	3.8
	$[C_3(NBuMe)_3]NO_3$	0.042	1106	172	6.4	1.4	0.011	42	16.7
	$[C_3(NBuMe)_3]TFSA$	0.048	1094	150	7.3	0.2	0.215	32	2.6
C_{2v}	$[C_3(NEt_2)_2NMe_2]DCA$	0.100	836	162	5.2	0.1	0.591	28	1.6
	$[C_3(NEt_2)_2NMe_2]TFSA$	0.058	1080	144	7.5	0.2	0.474	29	2.1
	$[C_3(NEt_2)_2NAllyl_2]TFSA$	0.056	1076	151	7.1	0.1	0.242	32	3.0
	$[C_3(NEt_2)_2NBu_2]DCA$	0.080	935	163	5.7	0.2	0.227	32	3.2
	$[C_3(NEt_2)_2NBu_2]TFSA$	0.051	1137	148	7.7	0.4	0.236	32	3.2
	$[C_3(NEt_2)_2NHex_2]DCA$	0.052	1067	157	6.8	0.1	0.135	33	4.0
	$[C_3(NEt_2)_2NHex_2]TFSA$	0.025	1409	135	10.5	0.3	0.130	34	4.2
	$[C_3(NEt_2)_2N(C_2H_4OH)_2]$ TFSA	0.074	1122	175	6.4	0.4	0.038	41	5.8
C_s	$[C_3(NEt_2)_2NBuMe]DCA$	0.102	837	166	5.0	0.1	0.389	29	2.3
	$[C_3(NEt_2)_2NBuMe]TFSA$	0.037	1251	136	9.2	0.2	0.310	31	2.3
	$[C_3(NEt_2)_2NHexH]TFSA$	0.056	1105	156	7.1	1.3	0.133	34	4.9
	$[C_3(NEt_2)_2NHexMe]DCA$	0.095	870	166	5.3	0.1	0.309	30	2.7
	$[C_3(NEt_2)_2NHexMe]TFSA$	0.069	1034	152	6.8	0.1	0.361	30	2.7

For the samples where both the viscosity and glass transition temperatures were obtained, a fragility plot was prepared (Figure 5.14) which is an Arrhenius plot that is scaled with the glass transition temperature. This plot shows the strong or fragile behaviour of a liquid.[28] Strong behaviour (those that do not deviate from Arrhenius behaviour) will lie on the 45° line shown. It is seen that all of these triaminocyclopropenium ionic liquids plotted show fragile behaviour and occur in a very similar region to other ionic liquids.[13]

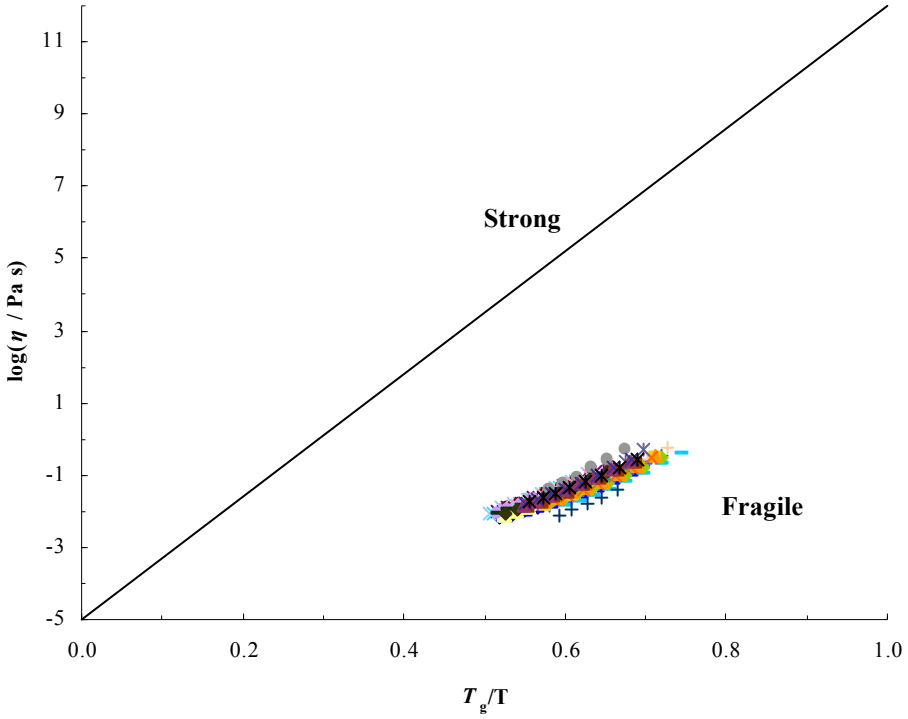


Figure 5.14 – T_g scaled Arrhenius plots of viscosity

5.5 Conductivity

Since ionic liquids are composed of charged molecules, they are conductive. In general, they show conductivity comparable to good non-aqueous electrolytes (~10 mS cm^{-1}), although less than many aqueous electrolytes. However, ionic liquids are generally composed of relatively large ions and there can be ion-pair formation. These factors will decrease the conductivity. As will be discussed later, the viscosity and conductivity transport properties are intrinsically linked and follow the same general trends.

The conductivity of triaminocyclopropenium salts are seen to be comparable to other ionic liquids (Table 5-6). For the low viscosity triaminocyclopropenium ionic liquids $[C_3(NEt_2)_3]$DCA and $[C_3(NEt_2)_2NMe_2]$DCA, the conductivity is 4.69 and 4.64 mS cm^{-1}, respectively, at 20 °C. As the temperature increases, conductivity also rapidly increases (Figure 5.15). For example, $[C_3(NEt_2)_3]$DCA and $[C_3(NEt_2)_2NMe_2]$DCA reach 26.33 and 27.21 mS cm^{-1}, respectively, at 90 °C.

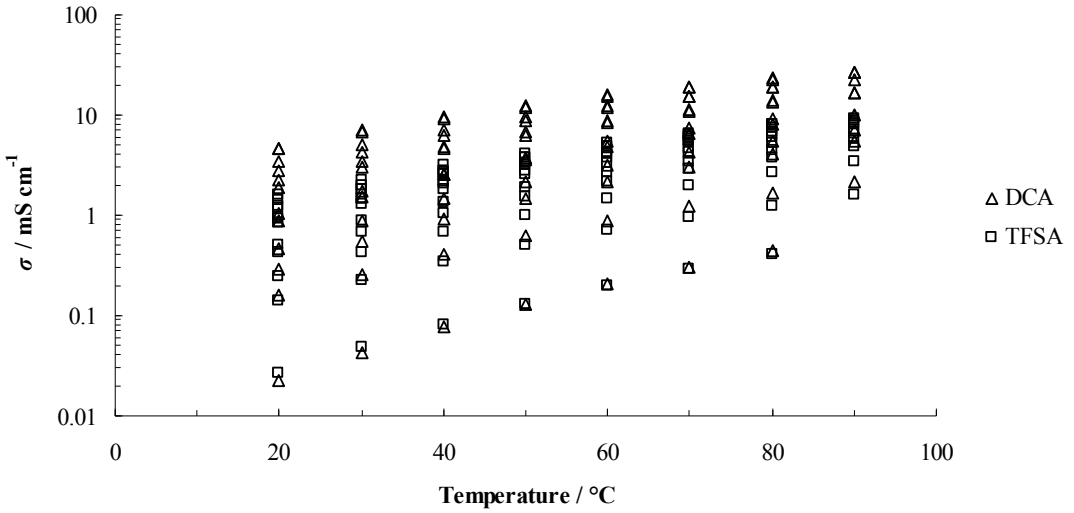


Figure 5.15 – Conductivity versus temperature for TFSA and DCA triaminocyclopropenium ILs

A larger cation size was seen to decrease conductivity (Figure 5.16). This is due to the charge carriers (the ions) not being able to move as easily when they or the rest of the solvent is composed of larger molecules. This is also the reason viscosity and conductivity are correlated, a higher viscosity will hinder the movement of charge carriers thus lowering conductivity. The trends within anion series are similar to the trends within the anion series of viscosity. The trends between anion series are not necessarily the same because the nature of the anion (such as size or specific interactions) can also a role in determining conductivity beyond influencing the viscosity. For example, $[C_3(NBu_2)_3]^+$, $[C_3(NPent_2)_3]^+$ and $[C_3(NHex_2)_3]^+$ have lower viscosity as the TFSA salt compared to the DCA salt, while also having lower conductivity as the TFSA salt than the DCA salt, although the differences are not large.

Table 5-6 – Summary of conductivity measurements

			σ / mS cm^{-1}							
		M_{cation} g mol^{-1}	20 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C
D_{3h}	$[C_3(NEt_2)_3]ClO4$	252	0.71	1.31	2.20	3.43	5.07	7.12	9.61	–
	$[C_3(NEt_2)_3]DCA$	252	4.688	6.797	9.199	11.965	15.137	18.630	22.397	26.332
	$[C_3(NEt_2)_3]TFSA$	252	1.387	1.983	2.755	3.681	4.752	5.972	7.349	8.857
	$[C_3(NPr_2)_3]DCA$	336	–	–	–	0.634	5.871	8.016	10.481	13.246
	$[C_3(NPr_2)_3]NO_3$	336	0.070	0.181	0.365	0.678	1.060	1.352	1.944	2.664
	$[C_3(NPr_2)_3]TFSA$	336	0.498	0.862	1.323	1.904	2.629	3.491	4.498	5.642
	$[C_3(NAllyl_2)_3]DCA$	324	0.879	1.562	2.525	3.818	5.424	7.349	9.235	–
	$[C_3(NAllyl_2)_3]TFSA$	324	0.927	1.472	2.192	3.099	4.164	5.424	6.826	8.397
	$[C_3(NBu_2)_3]BF_4$	420	0.084	0.173	0.315	0.532	0.842	1.262	1.795	2.453
	$[C_3(NBu_2)_3]Cl$	420	–	0.014	0.035	0.081	0.164	0.305	0.528	0.857
	$[C_3(NBu_2)_3]DCA$	420	0.469	0.876	1.437	2.178	3.112	4.243	5.572	7.055
	$[C_3(NBu_2)_3]NO_3$	420	0.07	0.16	0.32	0.59	0.97	1.57	2.34	–
	$[C_3(NBu_2)_3]OTf$	420	–	0.299	0.531	0.868	1.343	1.965	2.749	3.714
	$[C_3(NBu_2)_3]TFSA$	420	0.428	0.694	1.057	1.535	2.144	2.915	3.819	4.870
	$[C_3(NPent_2)_3]DCA$	504	0.30	0.54	0.91	1.44	2.14	3.03	4.12	5.40
	$[C_3(NPent_2)_3]TFSA$	504	0.25	0.42	0.67	1.01	1.45	2.00	2.67	3.45
	$[C_3(NHex_2)_3]DCA$	588	0.161	0.260	0.414	0.620	0.891	1.228	1.644	2.128
	$[C_3(NHex_2)_3]TFSA$	588	0.141	0.226	0.349	0.508	0.710	0.965	1.257	1.602
	$[C_3(NHex_2)_3]DBP$	924	0.02	0.04	0.08	0.13	0.21	0.31	0.44	–
	$[C_3(NDec_2)_3]DCA$	924	0.03	0.05	0.08	0.13	0.20	0.29	0.40	–
C_{3h}	$[C_3(NBuMe)_3]BF_4$	294	0.25	0.53	0.93	1.49	2.25	3.20	4.36	5.69
	$[C_3(NBuMe)_3]DCA$	294	1.92	3.09	4.56	6.35	8.48	0.90	13.62	16.60
	$[C_3(NBuMe)_3]TFSA$	294	0.94	1.45	2.07	2.83	3.71	4.72	5.87	7.12

			σ / mS cm^{-1}							
		M_{cation} g mol^{-1}	20 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C
C_{2v}	$[C_3(NEt_2)_2NMe_2]$DCA	224	4.64	6.97	9.54	12.44	15.70	19.25	23.13	27.21
	$[C_3(NEt_2)_2NMe_2]$TFSA	224	1.57	2.25	3.10	4.11	5.26	6.55	7.93	9.37
	$[C_3(NEt_2)_2NBu_2]$DCA	308	2.20	3.42	4.91	6.70	8.79	11.16	13.82	16.71
	$[C_3(NEt_2)_2NBu_2]$TFSA	308	0.85	1.29	1.85	2.53	3.35	4.28	5.35	6.52
	$[C_3(NEt_2)_2NHex_2]$DCA	364	1.03	1.71	2.57	3.64	4.94	6.46	8.21	10.16
	$[C_3(NEt_2)_2N(C_2H_4OH)_2]$TFSA	284	0.17	0.32	0.55	0.87	1.31	1.84	2.50	3.28
C_s	$[C_3(NEt_2)_2NBuMe]$DCA	266	3.50	5.12	7.13	9.50	12.20	15.24	18.60	22.16
	$[C_3(NEt_2)_2NBuMe]$TFSA	266	1.23	1.84	2.51	3.35	4.32	5.41	6.63	7.96
	$[C_3(NEt_2)_2NHexMe]$DCA	294	2.77	4.34	6.34	8.82	11.75	15.13	18.88	–
	$[C_3(NEt_2)_2NHexMe]$TFSA	294	1.18	1.82	2.65	3.69	4.94	6.38	8.03	–

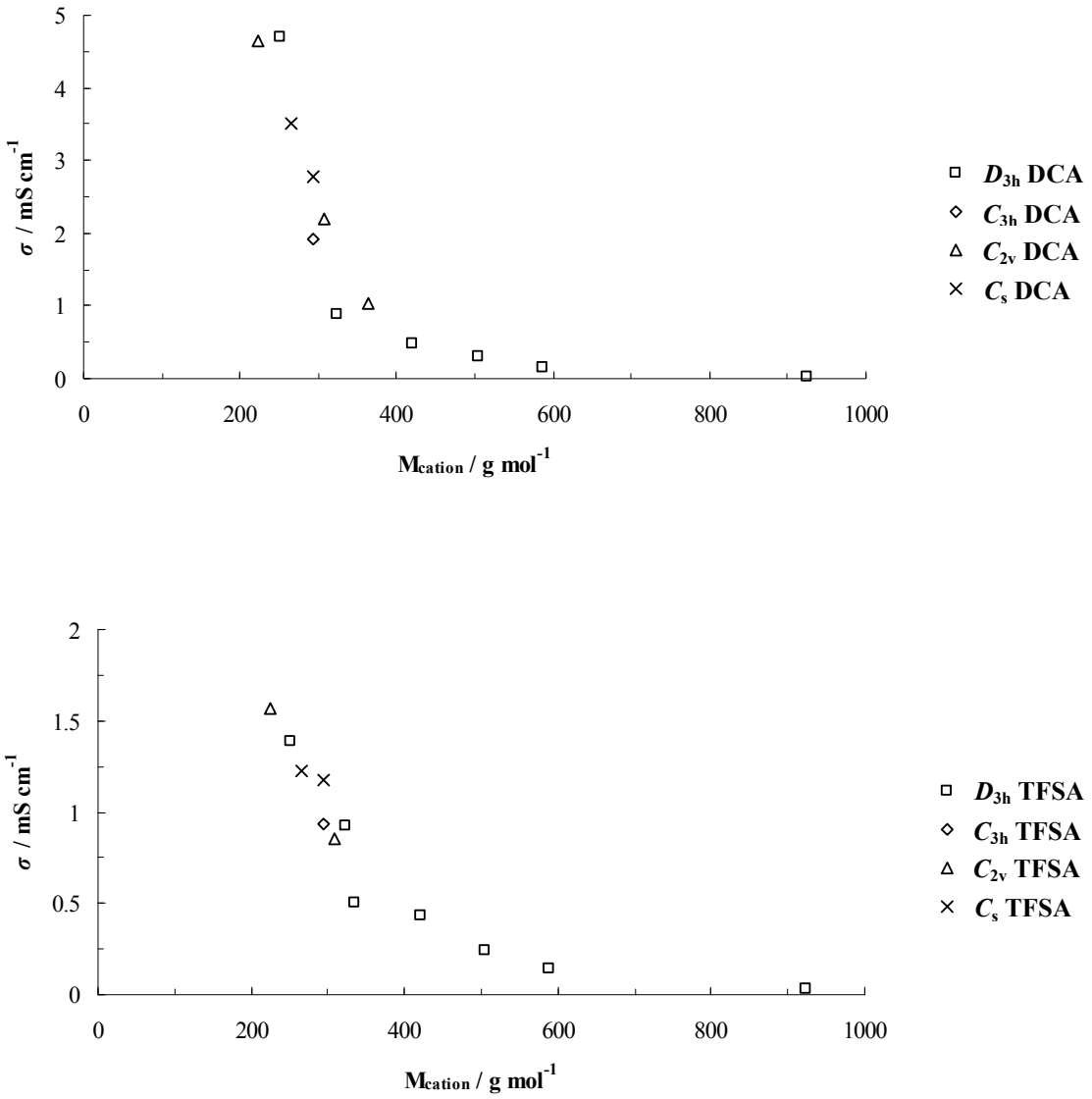


Figure 5.16 – Conductivity at 20 °C versus molecular weight of the cation, for DCA (top) and TFSA (bottom) salts with alkyl substituents

The data was also analysed to look for the alternating effect that has been observed in the viscosity data (Figure 5.17). The alternating effect is observed, again with some temperature and anion dependence, however, it is not as easily observed due to decreasing ionicity and overall curvature. As the cation size increases the ionicity decreases, and this decreases the conductivity. In the D_{3h} TFSA series (Figure 5.17a) $[C_3(NPr_2)_3]$TFSA has lower conductivity relative to its neighbours, which correlates with the higher viscosity observed. $[C_3(NPent_2)_3]$TFSA does not appear to have lower

conductivity, but at this point the ionicity is decreasing and will only decrease further as the alkyl chain length has increased, thus pulling the trend downwards. In the D_{3h} DCA series (Figure 5.17b) the alternating sequence is not clearly visible, although by comparison with the TFSA series relative differences are observed probably due to the alternating sequence.

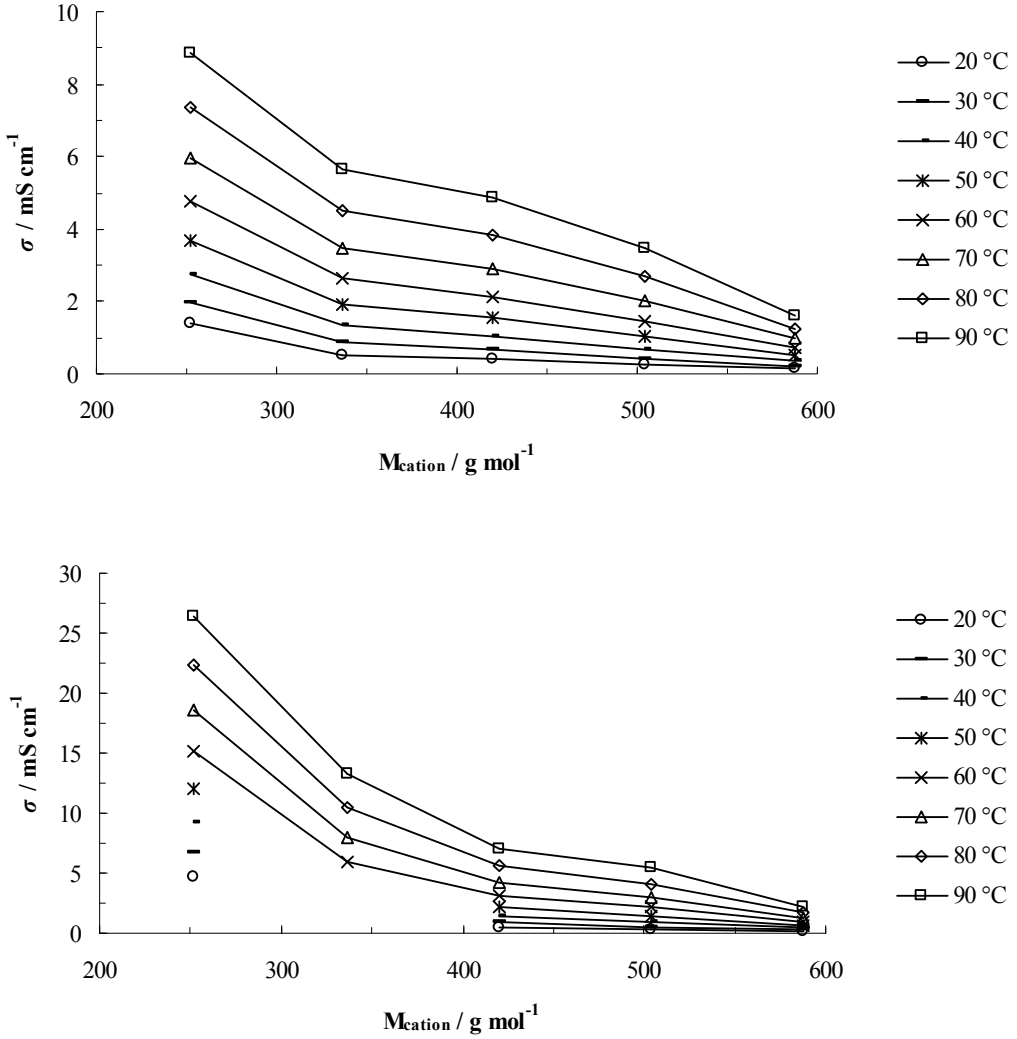


Figure 5.17 – D_{3h} C_n cations, n = 2-6 a) Top TFSA series. b) Bottom DCA series

As was done with the viscosity data, the conductivity data was fitted to the Vogel-Fulcher-Tammann (VFT) and Arrhenius empirical equations, Equation 6 and Equation 7, to model the temperature dependence of viscosity. The parameters were found by least

squares fitting, Table 5-7. The standard deviation of the data from the fitted model is also given, and from this it is seen that the VFT equation is more accurate then the fitting of the Arrhenius equation.

In the VFT equation (Equation 6), σ_∞, B and T_0 are constants. B and T_0 are equivalent to the parameters from the viscosity VFT equation, and are again used to calculate the parameter D, to measure fragility. Again, there are no strong trends of the VFT parameters identified for varying cations size or symmetry, however, there is a weak trend of a higher D value as molecular weight increases, as was the case with viscosity. With the anions series it is seen that B is higher and T_0 lower, and consequently D values are higher, for the TFSA salt than the corresponding DCA salt, i.e. less fragile, as was the case with viscosity. D values calculated using the conductivity data are seen to be consistently lower than those found with viscosity data, due to generally lower B and higher T_0 values.

$$\sigma = \sigma_\infty \exp\left(\frac{-B}{T - T_0}\right) = \sigma_\infty \exp\left(\frac{-DT_0}{T - T_0}\right)$$

Equation 6 – Vogel-Fulcher-Tammann (VFT) equation

The Arrhenius equation was also fitted to the conductivity data. As already mentioned this has a substantially higher standard deviation in the VFT equation, although it can still be used to model the viscosity within the 20 to 90 °C temperature range used. The activation energies for conductivity were determined to be between 22 and 63 kJ mol^{-1}, and had a relatively good correlation to those determined from viscosity ($R^2 = 0.93$)

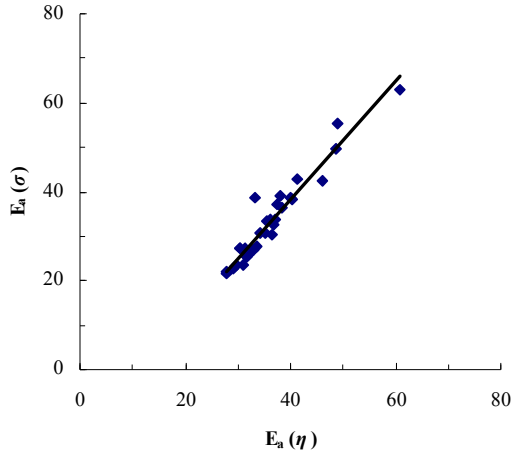


Figure 5.18 – Correlation between $E_a(\sigma)$ and $E_a(\eta)$

$$\sigma = A\exp\left(\frac{-E_a}{RT}\right)$$

Equation 7 – Arrhenius equation

Table 5-7 – Conductivity fitting parameters

		σ_∞	B	T_0	D	δ	A x10^{-4}	E_a	δ
		mS cm^{-1}	K	K		mS cm^{-1}	mS cm^{-1}	kJ mol^{-1}	mS cm^{-1}
D_{3h}	$[C_3(NEt_2)_3]ClO4$	1351	860	179	4.8	0.01	327	37	0.4
	$[C_3(NEt_2)_3]DCA$	481	546	175	3.1	0.03	3.60	22	0.7
	$[C_3(NEt_2)_3]TFSA$	439	846	146	5.8	0.01	2.16	23	0.2
	$[C_3(NPr_2)_3]DCA$	397	529	208	2.5	0.001	11.2	27	2.2
	$[C_3(NPr_2)_3]NO_3$	108	498	225	2.2	0.01	53600	55	0.1
	$[C_3(NPr_2)_3]TFSA$	213	639	188	3.4	0.02	13.7	30	0.2
	$[C_3(NAllyl_2)_3]DCA$	384	571	199	2.9	0.07	102	34	0.5
	$[C_3(NAllyl_2)_3]TFSA$	317	672	178	3.8	0.01	8.73	28	0.3
	$[C_3(NBu_2)_3]BF_4$	629	1026	178	5.8	0.003	340	42	0.1
	$[C_3(NBu_2)_3]Cl$	3193	1472	184	8.0	0.0004	110000	63	0.05
	$[C_3(NBu_2)_3]DCA$	258	588	200	2.9	0.01	58.1	34	0.4
	$[C_3(NBu_2)_3]NO_3$	1855	1168	178	6.6	0.01	6050	50	0.1
	$[C_3(NBu_2)_3]OTf$	759	993	177	5.6	0.002	128	38	0.1
	$[C_3(NBu_2)_3]TFSA$	812	1111	146	7.6	0.01	13.2	31	0.1
	$[C_3(NPent_2)_3]DCA$	712	914	176	5.2	0.01	109	36	0.4
	$[C_3(NPent_2)_3]TFSA$	472	984	163	6.0	0.002	22.9	33	0.1
	$[C_3(NHex_2)_3]DCA$	669	1292	138	9.3	0.01	11.5	33	0.1

		σ_∞ mS cm^{-1}	B K	T_0 K	D	δ mS cm^{-1}	A x10^{-4} mS cm^{-1}	E_a kJ mol^{-1}	δ mS cm^{-1}
D_{3h}	$[C_3(NHex_2)_3]$TFSA	241	1071	149	7.2	0.004	4.45	31	0.04
	$[C_3(NHex_2)_3]$DBP	460	1142	157	7.3	0.001	28.2	36	0.06
	$[C_3(NDec_2)_3]$DCA	354	1300	159	8.2	0.0004	98.0	43	0.01
	$[C_3(NDec_2)_3]$TFSA	317	1380	146	9.4	0.0001	24.5	39	0.01
C_{3h}	$[C_3(NBuMe)_3]BF_4$	295	629	204	3.1	0.01	247	39	0.3
	$[C_3(NBuMe)_3]$DCA	417	564	188	3.0	0.02	13.7	27	0.6
	$[C_3(NBuMe)_3]$TFSA	213	639	175	3.7	0.01	3.38	25	0.2
C_{2v}	$[C_3(NEt_2)_2NMe_2]$DCA	339	432	192	2.2	0.09	4.23	22	0.8
	$[C_3(NEt_2)_2NMe_2]$TFSA	248	647	166	3.9	0.02	1.76	23	0.2
	$[C_3(NEt_2)_2NBu_2]$DCA	414	583	182	3.2	0.02	7.94	25	0.5
	$[C_3(NEt_2)_2NBu_2]$TFSA	289	759	163	4.7	0.001	3.37	26	0.2
	$[C_3(NEt_2)_2NHex_2]$DCA	333	620	186	3.3	0.02	14.3	39	5.9
	$[C_3(NEt_2)_2N(C_2H_4OH)_2]$TFSA	314	806	186	4.3	0.006	87.3	37	0.2
C_s	$[C_3(NEt_2)_2NBuMe]$DCA	571	627	170	3.7	0.01	5.13	23	0.6
	$[C_3(NEt_2)_2NBuMe]$TFSA	228	659	167	4.0	0.02	1.95	23	0.2
	$[C_3(NEt_2)_2NHexMe]$DCA	756	647	178	3.6	0.01	22.7	27	0.5
	$[C_3(NEt_2)_2NHexMe]$TFSA	483	769	165	4.7	0.004	9.77	27	0.2

5.6 Ionicity

As has already been mentioned, conductivity and viscosity are linked. As viscosity decreases, it becomes easier for charge carriers to move, so conductivity increases. As with molecular liquid electrolytes, conductivity and viscosity of ionic liquids are usually linked through Walden's rule, Equation 8, conductivity and viscosity being inversely proportional to each other. Conductivity is often replaced with molar conductivity (Λ), to remove the effect of one liquid having a different number of charge carriers to another. The product of viscosity and molar conductivity is the Walden product, and this is inversely proportional to the ion size. It is also anion dependent. These dependencies are a reflection of the dependence of viscosity and conductivity on ion size and anions. For triaminocyclopropenium ionic liquids the Walden product (Table 5-8) is similar to many other classes of cation.[3] However, considering the large size of triaminocyclopropenium ionic liquids they are relatively high. This means they have good molar conductivities for a given viscosity compared to other ionic liquids, although, because of their larger size the conductivity is lower overall.

$$\Lambda\eta = \text{Walden product}$$

Equation 8 – Walden rule

Table 5-8 – Walden product, deviation from ideal and slope of Walden plot

		Walden product			
		20 °C	60 °C	ΔW	Slope
D_{3h}	$[C_3(NEt_2)_3]ClO_4$		0.85	0.07[a]	0.89
	$[C_3(NEt_2)_3]$DCA	0.95	0.71	0.02	0.80
	$[C_3(NEt_2)_3]$TFSA	0.55	0.40	0.26	0.81
	$[C_3(NPr_2)_3]$DCA		0.36	0.44[a]	0.88
	$[C_3(NPr_2)_3]NO_3$		0.60	0.22[a]	0.87
	$[C_3(NPr_2)_3]$TFSA	0.56	0.45	0.25	0.85
	$[C_3(NAllyl_2)_3]$DCA	0.70	0.58	0.15	0.89
	$[C_3(NAllyl_2)_3]$TFSA	0.56	0.44	0.25	0.85
	$[C_3(NBu_2)_3]BF_4$		0.40	0.40[a]	0.89
	$[C_3(NBu_2)_3]$Cl		0.55	0.26[a]	0.96
	$[C_3(NBu_2)_3]$DCA	0.71	0.67	0.15	0.95
	$[C_3(NBu_2)_3]NO_3$		0.75	0.13[a]	0.92
	$[C_3(NBu_2)_3]$OTf		0.19	0.73[a]	0.97
	$[C_3(NBu_2)_3]$TFSA	0.61	0.52	0.21	0.89
	$[C_3(NPent_2)_3]$DCA	0.56	0.54	0.25	0.96
	$[C_3(NPent_2)_3]$TFSA	0.48	0.45	0.32	0.95
	$[C_3(NHex_2)_3]$DCA	0.38	0.31	0.42	0.90
	$[C_3(NHex_2)_3]$TFSA	0.32	0.27	0.50	0.91
	$[C_3(NHex_2)_3]$DBP	0.20	0.19	0.69	0.97
	$[C_3(NDec_2)_3]$DCA	0.14	0.15	0.86	1.02
	$[C_3(NDec_2)_3]$TFSA	0.13	0.14	0.88	1.02
C_{3h}	$[C_3(NBuMe)_3]$DCA	0.71	0.54	0.15	0.84
	$[C_3(NBuMe)_3]$TFSA	0.45	0.34	0.35	0.82
C_{2v}	$[C_3(NEt_2)_2NMe_2]$DCA	0.77	0.60	0.11	0.81
	$[C_3(NEt_2)_2NMe_2]$TFSA	0.51	0.37	0.30	0.79
	$[C_3(NEt_2)_2NBu_2]$DCA	0.88	0.67	0.05	0.82
	$[C_3(NEt_2)_2NBu_2]$TFSA	0.52	0.38	0.29	0.82
	$[C_3(NEt_2)_2NHex_2]$DCA	0.60	0.51	0.22	0.87
	$[C_3(NEt_2)_2N(C_2H_4OH)_2]$TFSA		0.54	0.27[a]	0.85
C_s	$[C_3(NEt_2)_2NBuMe]$DCA	0.86	0.64	0.07	0.81
	$[C_3(NEt_2)_2NBuMe]$TFSA	0.56	0.41	0.25	0.78
	$[C_3(NEt_2)_2NHexMe]$DCA	0.87	0.75	0.06	0.90
	$[C_3(NEt_2)_2NHexMe]$TFSA	0.58	0.50	0.23	0.89

Note: [a] 60 °C

From Walden's rule, we can construct a Walden plot, log(Λ) versus log(1/η), Figure 5.19. 1/η is also known as fluidity. The ideal line has been added, running at 45°, which represents data for dilute aqueous KCl solutions which displays ideal behaviour because there is no association between the ions. Walden plots will give an indication of ionicity,[29] which Watanabe and Angell *et al.*[30] define as "the degree to which a liquid, comprised of charged particles, behaves as a collection of completely free ions, each surrounded by a uniform density of ions of the opposite charge." Ionic liquids fall below the ideal line because of correlations between ions, such as ion pairing or larger aggregates of ions. Ion pairing forms a neutral species which does not carry charge, and larger aggregates, while possibly being charged, will not move as easily, thus lowering conductivity without largely affecting viscosity. Thus, these correlations will cause deviation from Nernst-Einstein behaviour, which means the distance from the ideal line on a Walden plot (ΔW) gives an indication of the ionicity of the liquid. Angell *et al.*[31] has suggested that Walden plots can be useful in classifying ionic liquids, with those above the ideal line being superionic liquids, those near (less than one order of magnitude below the ideal line) being good ionic liquids and those far below the line being poor ionic liquids. Using this classification, all the triaminocyclopropenium ionic liquids reported here can be classed as good ionic liquids. It is interesting to note that deviation from ideal behaviour is linked to vapour pressures:[32] as more ion pairing and aggregation occurs (increasing ΔW), vapour pressures are higher because these same correlations are needed for vapourisation to occur.[33]

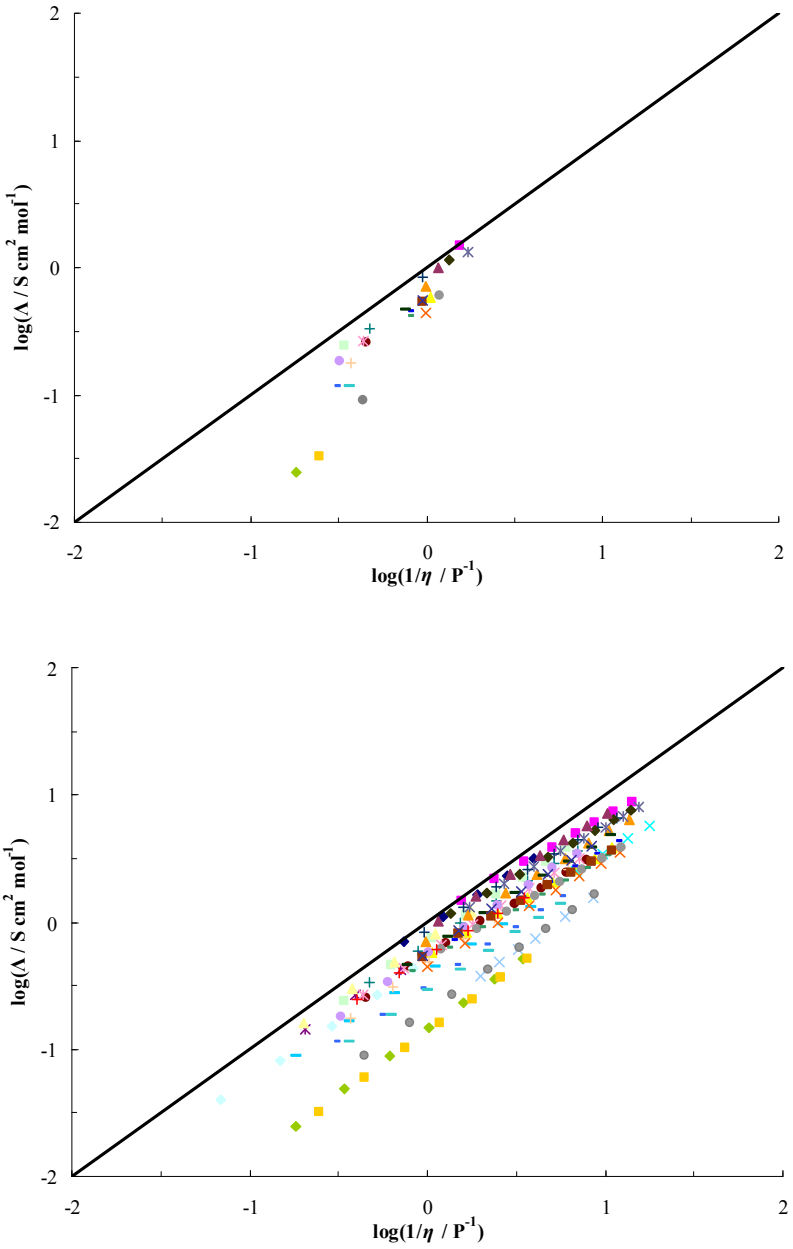


Figure 5.19 – Walden plots a) 20 °C b) 20 - 90 °C, or available data

Triaminocyclopropenium ionic liquids are seen to fall below the ideal line (Figure 5.20), in a similar region to other ionic liquids.[3] The deviation[29] from ideal behaviour for triaminocyclopropenium ionic liquids (Table 5-8), is dependent on both the type of anion and the cation size. The anion series, from least to most deviation from ideal behaviour, is DCA < ClO_4, NO_3 < TFSA, Cl < BF_4 < OTf.

When the cations are smaller than $[C_3(NBu_2)_3]^+$ little size dependence is seen. As the cations get larger, the deviation from ideal behaviour increases (Figure 5.20). For example, ΔW for $[C_3(NBu_2)_3]$DCA is 0.15 at 20 °C, and this increases to 0.25, 0.42 and 0.86 for $[C_3(NPent_2)_3]$DCA, $[C_3(NHex_2)_3]$DCA and $[C_3(NDec_2)_3]$DCA, respectively. These large cations show increasing deviation because ion pairing is increasing, as cations get larger it forces ions apart which prevents the relatively small anions from interacting with as many cations, so increasing its electrostatic attraction to one cation. The lower ionicity suggested by a large ΔW, along with a medium-high viscosity of the liquid, accounts for the lower conducitivity of these large cations. It is still noteworthy that even at these large cation sizes, ΔW is still less than one, so they still show reasonable ionicity. The good ionicity of triaminocyclopropenium ionic liquids, combined with relatively large molecular weights compared to other ionic liquids, means that low vapour pressures can be expected, although since other ionic liquids already have low vapour pressures, the differences may not be useful.

Symmetry dependence was not observed, but the less symmetric cations used are all relatively small, and symmetry dependence might be seen if larger less-symmetric cations are investigated.

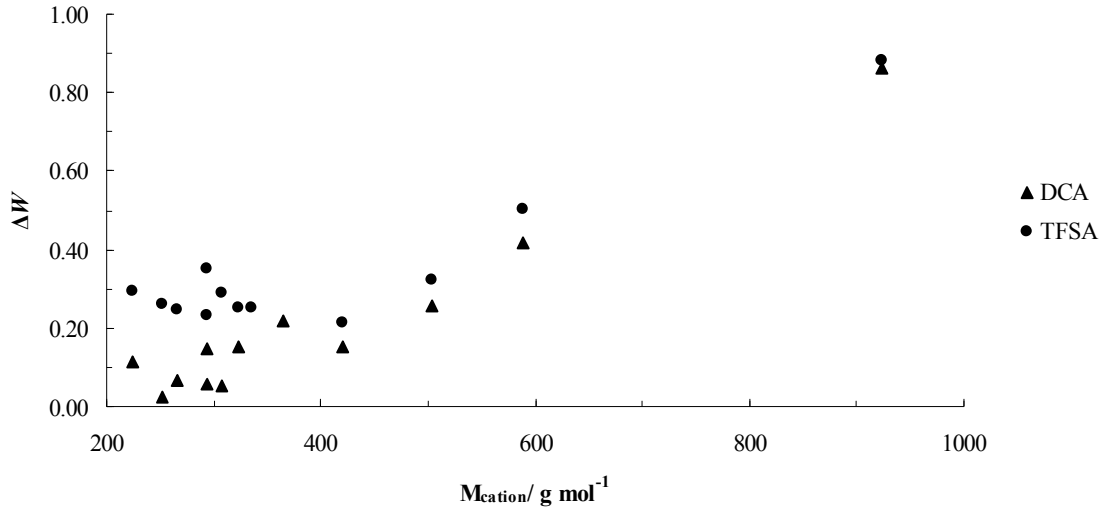


Figure 5.20 – ΔW at 20 °C versus cation size for DCA and TFSA series

It is interesting to note the ΔW for $[C_3(NEt_2)_2N(C_2H_4OH)_2]$TFSA is 0.27, at 60 °C, similar to other small triaminocyclopropenium TFSA salts. Since ionicity of this ionic liquid is unaffected by the hydrogen bonds, these must be predominantly inter molecular hydrogen bonds to all surrounding ions, rather than to one anion, which in that case would form a stronger ion pair. These inter molecular hydrogen bonds then increase both the viscosity and conductivity, but do not affect ionicity.

Figure 5.19b shows the Walden plot for all samples over their measured temperature range, usually 20 to 90 °C. It is seen that many of the series do not have a slope of 1 (Table 5-8), and this is because ionicity can decrease with temperature,[31] so the Walden product is not constant with temperature for these liquids. It is also observed that this slope is dependent on the size of the cation, with small cations having a slope of approximately 0.8, while the larger $[C_3(NDec_2)_3]^+$ cations have a slope of 1. Angell *et al.*[31] puts the increasing deviation down to correlations between anions and cations, which would be more difficult with a large size mismatch.

It should be noted that a Walden plot does not take the size of ions into account when setting the ideal behaviour. MacFarlane *et al.*[29] has used a modified Walden plot (of Equation 9) taking into account of the effective ion size, and this decreases ΔW. The same would occur for triaminocyclopropenium ILs. However, the unmodified Walden plot used in this work is still extensively used to obtain qualitative information about ionicity.

$$\Lambda = \text{constant}\,\eta^{-1}\left(\frac{1}{r^+}+\frac{1}{r^-}\right)$$

Equation 9 – Modified Walden rule

Diffusion of individual species was investigated on a sample of $[C_3(NBu_2)_3]$TFSA, using pulsed field gradient NMR, by Paul M. Bayley at Monash University, Melbourne. This determined D_{cation} to be 3.17 x 10^{-12} m^2s^{-1}, and D_{anion} to be 5.62 x 10^{-12} m^2s^{-1}, Table 5-9. These are quite low, due to the high viscosity and large ion size, as would be expected by considering the Stokes-Einstein equation, Equation 10. In many ionic liquids, D_{cation} is

larger than D_{anion}, however, the large size of $[C_3(NBu_2)_3]^+$ causes D_{cation} to be smaller than D_{anion}.

Using the diffusions in the Nernst-Einstein equation (Equation 11), the molar conductivity (Λ_{NE}) can be calculated from the diffusions. When Λ_{NE} is compared to the measured molar conductivity (Λ_M), more quantitative information about the ionicity can be obtained. There are multiple ways of defining the deviation of Λ_M from Λ_{NE}. An ionicity plot of $\log(\Lambda_M)$ versus $\log(\Lambda_{NE})$ can be used to calculate ΔI, in the same way ΔW is found. For $[C_3(NBu_2)_3]$TFSA, ΔI was found to be 0.10. The deviation of Λ_M from Λ_{NE} can also be defined by $\Delta = 1 - \frac{\Lambda_M}{\Lambda_{NE}}$. Δ for $[C_3(NBu_2)_3]$TFSA was found to be 0.21. Both ΔI and Δ, mean that there was a 21% reduction in molar conductivity due ion correlations, or put another way: 79% ionicity. This is less than the reduction suggested by the ΔW of 0.21, which if applied quantitatively has ionicity of 62%. A Δ of only 0.21 shows very good ionicity, higher than the TFSA salts of 1-butyl-3-methylimdazolium (Δ = 0.37), *N*-butyl-*N,N,N*-trimethylammonium (Δ = 0.35), 1-butylpyridinium (Δ = 0.37) and *N*-butyl-*N*-methylpyrrolidinium (Δ = 0.30).[6,14-16,34] Watanabe *et al.*[6] has seen that the $E_T(30)$ solvent parameter is inversely related to the ionicity, and the $E_T(30)$ is mainly affected by the electron accepting ability and hydrogen bond interactions of the solvent. By comparison with the previously mentioned TFSA salts, the low Δ of $[C_3(NBu_2)_3]$TFSA suggests a low $E_T(30)$ would be expected – meaning weak electron accepting ability and hydrogen bond interactions. This correlates well with the triaminocyclopropenium cation being relatively electron rich, so has less Lewis acidicity. The idea of a less associating ionic liquid fits well with the higher ionicity of triaminocyclopropenium ILs. More diffusion data of triaminocyclopropenium salts would confirm whether triaminocyclopropenium ILs have good ionicity and are less associating in general or if $[C_3(NBu_2)_3]$TFSA is a specific case.

$$D_i = \frac{kT}{6\pi\eta r_i}$$

Equation 10 – Stokes-Einstein equation

$$\Lambda_{NE} = \frac{N_A e^2}{kT}\left(D_{cation} + D_{anion}\right)$$

Equation 11 – Nernst-Einstein eauation for a 1:1 salt

Watanabe *et al.*[6,35] have also used the concept of effective ion concentration, C_{eff}, which is suggested to reflect the strength of Coulombic interactions. C_{eff} is found by adjusting the concentration for the less than total ionicity. For $[C_3(NBu_2)_3]$TFSA, C_{eff} is 0.0013 mol cm^{-3}, which is lower than other ionic liquids, such as $[C_4MIM]$TFSA which has a C_{eff} of 0.0021 mol cm^{-3}. This is due to the low concentration resulting from the high molecular weight of $[C_3(NBu_2)_3]$TFSA, which is only partially offset by the high ionicity. With only one C_{eff} measured, it is not possible to draw conclusions about trends or the applicability of C_{eff}.

Table 5-9 – Diffusion data of $[C_3(NBu_2)_3]$TFSA at 20 °C

	D_{cation} / m^2 s^{-1}	D_{anion} / m^2 s^{-1}	Λ_{NE} / S cm^2 mol^{-1}	Λ_M / S cm^2 mol^{-1}	Δ	ΔI	ΔW	C_{eff} / mol cm^{-3}
$[C_3(NBu_2)_3]$TFSA	3.17 x 10^{-12}	5.62 x 10^{-12}	0.336	0.265	0.21	0.10	0.21	0.0013

5.7 Stability

As a new class of ionic liquid, the stability of triaminocyclopropenium ionic liquids is an important factor in determining their potential. The stability of a compound that is to be used in any kind of application, especially one that is ideally used repeatedly, is very important to allow for continued operation. Three aspects to stability of triaminocyclopropenium ionic liquids have been investigated: thermal, chemical and electrochemical stability.

5.7.1 Thermal stability

Thermal stability was investigated using thermal gravimetric analysis (TGA). TGA monitors the weight of a sample while the temperature is changed under a controlled atmosphere. The instrument used in this work was a simultaneous TGA-DSC, so heat flow information was obtained at the same time, although this is less accurate than the DSC data discussed previously and does not operate in sub ambient conditions.

An example of the TGA of $[C_3(NBu_2)_3]$TFSA at a 10 °C min^{-1} heating rate is shown (Figure 5.21). It is seen that while the temperature is low no substantial weight loss is observed, being at 99% of starting weight at 293 °C, and then once weight loss starts it continues at an increasing rate and completes decomposition in one step. Some samples did not drop to 0% weight, as residual charred material remained in the pan (this could be removed by heating under an oxidizing atmosphere). The decomposition points are reported as the onset temperatures, in this case 403 °C, taken from the greatest and least slope, and is therefore an over estimation of the thermal stability. The onset temperature is used because it is easily obtainable and comparable between samples, so the relative stability can be determined. The position of this onset temperature is affected by the heating rate that is used, and relatively fast heating rates such as 10 °C min^{-1} will increase the observed onset temperature.[36-38] For each sample, two heating rates were investigated: 10 °C min^{-1} and 1 °C min^{-1}. The atmosphere that TGA is carried out under is also an important parameter – in this work dry, N_2 gas was used as an inert atmosphere.

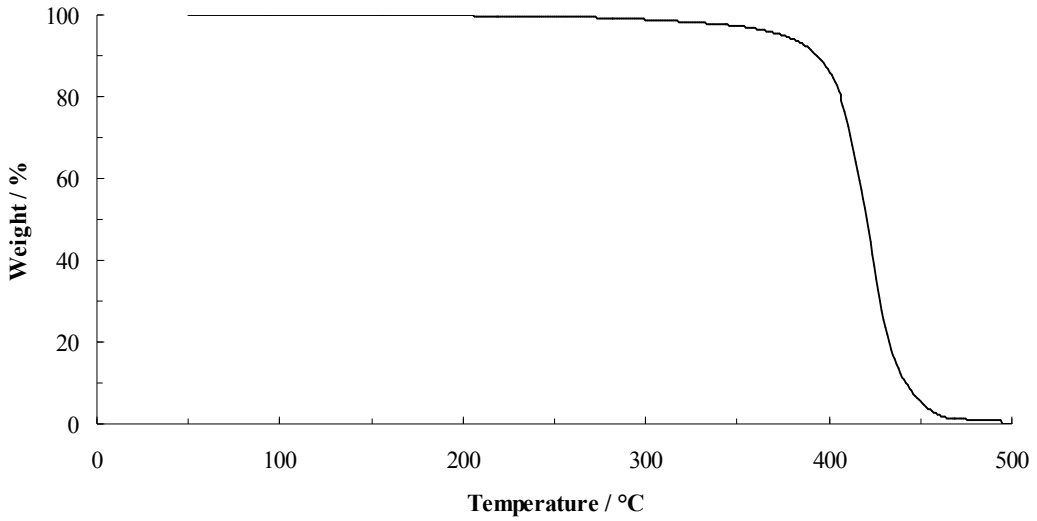


Figure 5.21 – TGA of $[C_3(NBu_2)_3]$TFSA at 10 °C min^{-1}

The thermal decomposition onset temperatures, T_d, at heating rates of 1 and 10 °C min^{-1} are shown (Table 5-10 and Figure 5.22). The T_d obtained with the different heating rates are consistent, with the T_d from 1 °C min^{-1} approximately 30 to 50°C lower. The highest onset temperature at 10 °C min^{-1} is 413 °C for $[C_3(NPr_2)_3]$TFSA.

The most notable trend is the anion dependence of T_d, for example the onset temperature increases from 265 °C for $[C_3(NEt_2)_3]NO_3$ to 393 °C for the TFSA salt. The general order from least stable to most stable is ClO_4, Br, Cl, NO_3 < SCN < DCA < OTf, BF_4 < TFSA. In terms of the cation, nearly all decomposition onset temperatures for a particular anion are within a 40°C range, showing that symmetry and alkyl chain length do not play a large role in determining the decomposition temperature. There are exceptions that do not fall within the 40 °C range. The $[C_3(NMe_2)_3]^+$ cation has onset temperatures noticeably lower for both the chloride and TFSA salts, 221 and 339 °C respectively, this is thought to be due to the lack of steric protection of the central cyclopropenium ring. Although, it is interesting to note that methyl groups on other cations do not result in lower onset temperatures, perhaps due to longer chains also being present and providing steric protection.

Allyl groups markedly lowered the decomposition onset temperatures, for example, lowering the decomposition temperature from 413 °C for $[C_3(NPr_2)_3]$TFSA to 306 °C for $[C_3(NAllyl_2)_3]$TFSA. $[C_3(NAllyl_2)_3]^+$ samples were seen to decompose via a two-step decomposition, where 10 to 15% of the sample weight was lost at the initial decomposition (the reported T_d), and the rest lost at a later decomposition, which could be almost immediately. The first decomposition event was exothermic, and it is thought to be polymerization occurring, involving the allyl side chains and possibly the cyclopropenium cation itself.

Alcohol groups also lowered the decomposition onset temperatures, for example, lowering the decomposition temperature from 393 °C for $[C_3(NEt_2)_3]$TFSA to 267 °C for $[C_3(NEt_2)_2N(C_2H_4OH)_2]$TFSA.

Table 5-10 – Thermal decomposition onset temperatures

			T_d / °C	
		M_{cation} g mol^{-1}	10 °C min^{-1}	1 °C min^{-1}
D_{3h}	$[C_3(NMe_2)_3]Cl$	168	221	179
	$[C_3(NMe_2)_3]$TFSA	168	339	309
	$[C_3(NEt_2)_3]BF_4$	252	372	344
	$[C_3(NEt_2)_3]Cl$	252	306	273
	$[C_3(NEt_2)_3]ClO_4$	252	274	241
	$[C_3(NEt_2)_3]$DCA	252	330	291
	$[C_3(NEt_2)_3]NO_3$	252	265	230
	$[C_3(NEt_2)_3]$SCN	252	311	283
	$[C_3(NEt_2)_3]$TFSA	252	393	349
	$[C_3(NC_5H_{10})_3]BF_4$	288	333	–
	$[C_3(NC_5H_{10})_3]Cl$	288	285	–
	$[C_3(NC_5H_{10})_3]NO_3$	288	273	253
	$[C_3(NAllyl_2)_3]Br$	324	241	222
	$[C_3(NAllyl_2)_3]Cl$	324	286	227
	$[C_3(NAllyl_2)_3]$DCA	324	270	235
	$[C_3(NAllyl_2)_3]$TFSA	324	306	278
	$[C_3(NPr_2)_3]BF_4$	336	397	287
	$[C_3(NPr_2)_3]Cl$	336	310	278
	$[C_3(N\textit{i}Pr_2)_3]Cl$	336	277	–

			T_d / °C	
		M_{cation} g mol^{-1}	10 °C min^{-1}	1 °C min^{-1}
D_{3h}	$[C_3(NPr_2)_3]$DCA	336	317	285
	$[C_3(NPr_2)_3]NO_3$	336	301	286
	$[C_3(NPr_2)_3]$TFSA	336	413	364
	$[C_3(NBu_2)_3]$BF4	420	388	330
	$[C_3(NBu_2)_3]$Br	420	318	281
	$[C_3(NBu_2)_3]$Cl	420	303	264
	$[C_3(NBu_2)_3]$DCA	420	337	293
	$[C_3(NBu_2)_3]$NO3	420	234	220
	$[C_3(NBu_2)_3]$OTf	420	390	346
	$[C_3(NBu_2)_3]$TFSA	420	403	351
	$[C_3(NPent_2)_3]$Cl	504	305	261
	$[C_3(NPent_2)_3]$DCA	504	321	292
	$[C_3(NPent_2)_3]$TFSA	504	395	343
	$[C_3(NHex_2)_3]$Cl	588	300	261
	$[C_3(NHex_2)_3]$DCA	588	321	291
	$[C_3(NHex_2)_3]$TFSA	588	406	346
	$[C_3(NHex_2)_3]$DBP	588	266	223
	$[C_3(NDec_2)_3]$Cl	924	293	259
	$[C_3(NDec_2)_3]$DCA	924	321	276
	$[C_3(NDec_2)_3]$TFSA	924	401	349
	$[C_3(N(C_2H_4OH)_2)_3]$Cl	348	226	190
C_{3h}	$[C_3(NBuMe)_3]$BF4	294	374	332
	$[C_3(NBuMe)_3]$Cl	294	293	262
	$[C_3(NBuMe)_3]$DCA	294	338	291
	$[C_3(NBuMe)_3]$NO3	294	291	258
	$[C_3(NBuMe)_3]$SCN	294	308	275
	$[C_3(NBuMe)_3]$TFSA	294	398	349
	$[C_3(NC_{18}Me)_3]$Cl	882	278	244
	$[C_3(NC_{18}Me)_3]$DCA	882	279	241
	$[C_3(NC_{18}Me)_3]$TFSA	882	384	338
C_{2v}	$[C_3(NEt_2)_2NMe_2]$DCA	224	322	293
	$[C_3(NEt_2)_2NMe_2]$TFSA	224	379	340
	$[C_3(NEt_2)_2NAllyl_2]$TFSA	276	358	292
	$[C_3(NEt_2)_2NBu_2]$DCA	308	334	302
	$[C_3(NEt_2)_2NBu_2]$TFSA	308	403	355
	$[C_3(NEt_2)_2NHex_2]$DCA	364	348	304
	$[C_3(NEt_2)_2NHex_2]$TFSA	364	396	356
	$[C_3(N^iPr_2)_2NBu_2]$Cl	364	292	262
	$[C_3(N^iPr_2)_2NBu_2]$DCA	364	332	302
	$[C_3(N^iPr_2)_2NBu_2]$TFSA	364	342	290

			T_d / °C	
		M_{cation} g mol^{-1}	10 °C min^{-1}	1 °C min^{-1}
C_{2v}	$[C_3(NEt_2)_2N(C_2H_4OH)_2]$TFSA	284	267	235
	$[C_3(NEt_2)_2N(C_2H_4OH)_2]$DCA	284	217	176
C_s	$[C_3(NEt_2)_2NBuMe]$TFSA	266	384	341
	$[C_3(NEt_2)_2NHexH]$TFSA	280	371	327
	$[C_3(NEt_2)_2NHexMe]$DCA	294	342	301
	$[C_3(NEt_2)_2NHexMe]$TFSA	294	398	351

Another sample that does not fall within a similar range of salts with the same anion is $[C_3(N^iPr_2)_2NBu_2]$TFSA. However, this T_d is not an accurate measure of its decomposition because the sample was contaminated with a high level of chloride ions, 2500ppm or approximately 4.5% of total anions. The chloride and DCA salts have similar decomposition temperatures to their respective anion series, showing that four isopropyl groups do not provide greater steric protection than four ethyl groups.

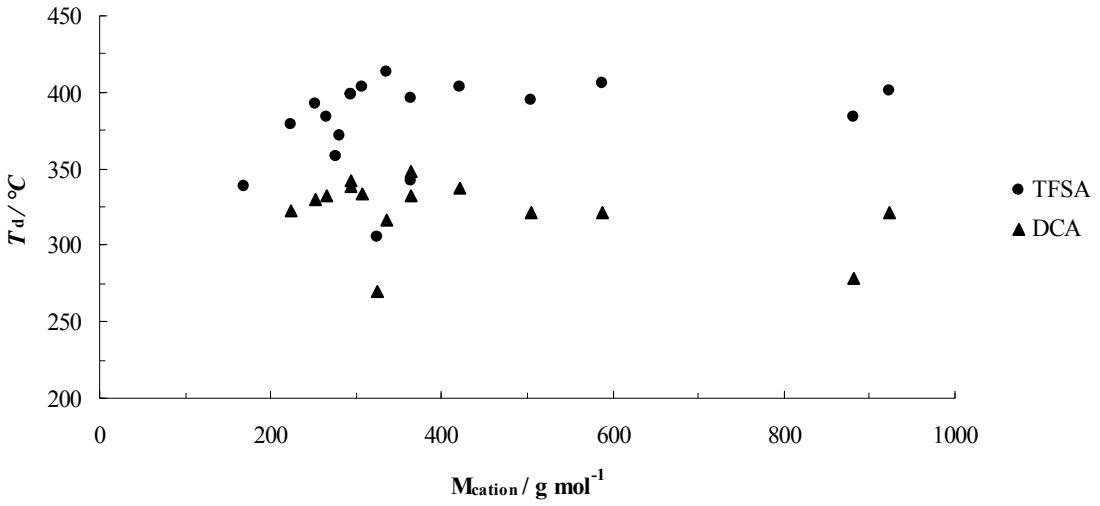


Figure 5.22 – Thermal decomposition onset temperature versus molecular weight of cation for TFSA and DCA salts

It was observed that all DCA salts produced an exothermic peak in the DSC upon decomposition. This is attributed to the trimerisation of the DCA anion,[38,39] which has been seen to occur at a similar temperature to the decomposition seen here. When the DCA anion is combined with the $[C_3(NAllyl_2)_3]^+$ cation, which also exhibits exothermic

decomposition as discussed previously, a very exothermic decomposition is seen. With a heating rate of 10 °C min^{-1} (Figure 5.23), at 270 °C a very exothermic reaction occurred that caused the sample to expand out of the pan and the temperature to momentarily increase to 325 °C. There is also a low shoulder with an onset temperature of 413 °C, which suggests a two step decomposition process, and does not fully decompose, with 17% weight still remaining. A repeated experiment produced similar results. Due to the loss of sample and the uncontrollable temperature increase the enthalpy of reaction was not valid. With a heating rate of 1 °C min^{-1} a two step decomposition process was seen (Figure 5.23). The reaction that occurs at 235 °C is equivalent to that which occurs at 270 °C in the previous experiment, although this time the reaction does not proceed uncontrollably. The enthalpy of reaction was calculated to be 720 kJ mol^{-1} (1850 J g^{-1}), although it is recognized that this type of reaction may be outside of the instruments operating conditions. A second decomposition step with an onset temperature of 379 °C then occurs. The weight percentage only decreases to 36% at 600 °C, with the remainder being a charred foam. Besides the trimerisation of DCA, the first reaction at 235 °C also must involve $[C_3(NAllyl_2)_3]^+$, either reacting with itself (allyl groups or triaminocyclopropenium core) or DCA, or a combination of these species.

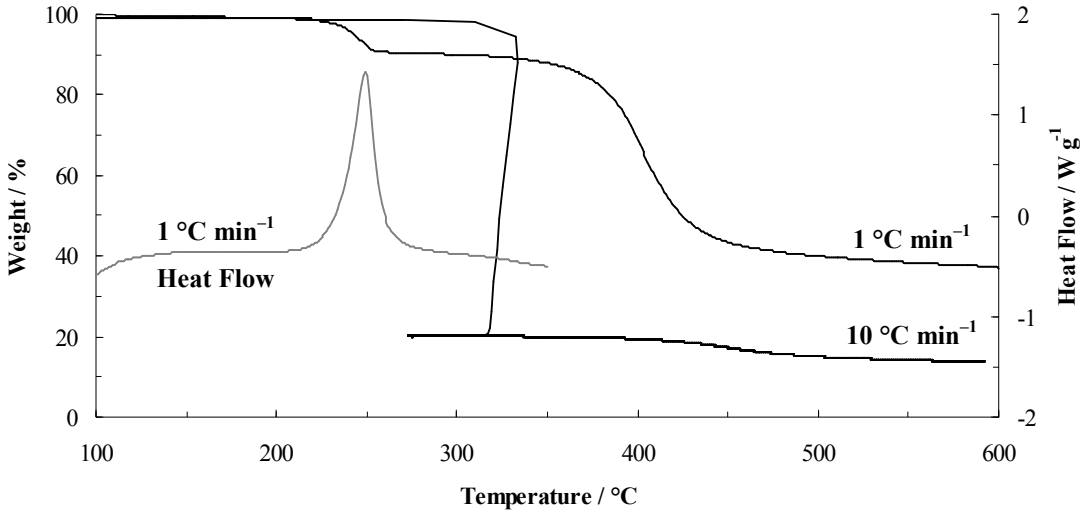


Figure 5.23 – TGA and DSC of $[C_3(NAllyl_2)_3]$DCA at 10 °C min^{-1} and 1 °C min^{-1}

The most important result from these TGA studies is that triaminocyclopropenium ionic liquids are thermally stable. Doubts had been raised that such a strained ring such as cyclopropenium would have good thermal stability. A comparison with decomposition temperatures for imidazolium ionic liquids (onset temperatures at 10 °C min^{-1} heating rate) shows triaminocyclopropenium ionic liquids to have similar thermal stability. Table 5-11 compares $[C_4MIM]^+$ (Fredlake *et al.*[7]), $[bmpy]^+$ (Crosthwaite *et al.*[40]) and $[p_{1,4}]^+$ (Wooster *et al.*[38]) with $[C_3(NBu_2)_3]^+$ triaminocyclopropenium salts. In the case of smaller, more coordinating anions $[C_3(NBu_2)_3]^+$ has a higher decomposition temperature than the imidazolium, pyridinium or pyrrolidinium (a quarternary ammonium cation) ionic liquids, but for the larger, less coordinating anions such as TFSA, $[C_4MIM]^+$ and $[p_{1,4}]^+$ are more thermally stable. If thermal stability is related to coordinating ability of the cation too, then this suggests triaminocyclopropenium ionic liquids are less coordinating.

Table 5-11 – Comparison of onset T_d

	T_d / °C			
Anion	$[C_4MIM]^+$	$[C_3(NBu_2)_3]^+$	$[C_4Mpy]^+$	$[p_{1,4}]^+$
Cl	264	303		
Br	273	318	235	
DCA	300	337		319
BF_4	361	388	364	
OTf	392	390		
TFSA	422	403	393	435

The onset temperature T_d is a reasonable measure for comparing relative stabilities, although it is an not accurate measure of long-term thermal stability. To gain an understanding of the long-term thermal stability of triaminocyclopropenium ionic liquids, the isothermal stability of $[C_3(NBu_2)_3]$TFSA was assessed at a number of temperatures under dry nitrogen and air atmospheres. Decomposition of ionic liquids is zero order,[41] and so the rate constant of decomposition is simply the gradient of a weight versus time plot. From the rate constant the time taken for 1% of the sample to decompose, $t_{0.99}$, is found. When $t_{0.99}$ is plotted against temperature and fitted with an exponential function, the temperature for 1% decomposition for any given time can be extrapolated or interpolated (Figure 5.24). Table 5-12 compares the temperature at which 1% decomposition occurs in 10 hours, $T_{0.01/10}$, for $[C_3(NBu_2)_3]^+$ with that of $[p_{1,4}]^+$[38] and

[C_2MIM]TFSA.[41] All $T_{0.01/10}$ values are substantially lower, and the triaminocyclopropenium salts are less thermally stable than the imidazolium or ammonium salts. While [$C_3(NBu_2)_3$]TFSA is less stable than [C_2MIM]TFSA or [$p_{1,4}$]TFSA, there is still a wide liquid range at which it is stable, 180 °C if under the nitrogen atmosphere or 140 °C if in an air atmosphere. [$C_3(NBu_2)_3$]DCA has a liquid range of approximately 100 °C. It should be mentioned, however, that these liquid ranges could be smaller in other circumstances depending on the environment and impurities in the ionic liquid, as factors such as water or halide impurities also play a role.

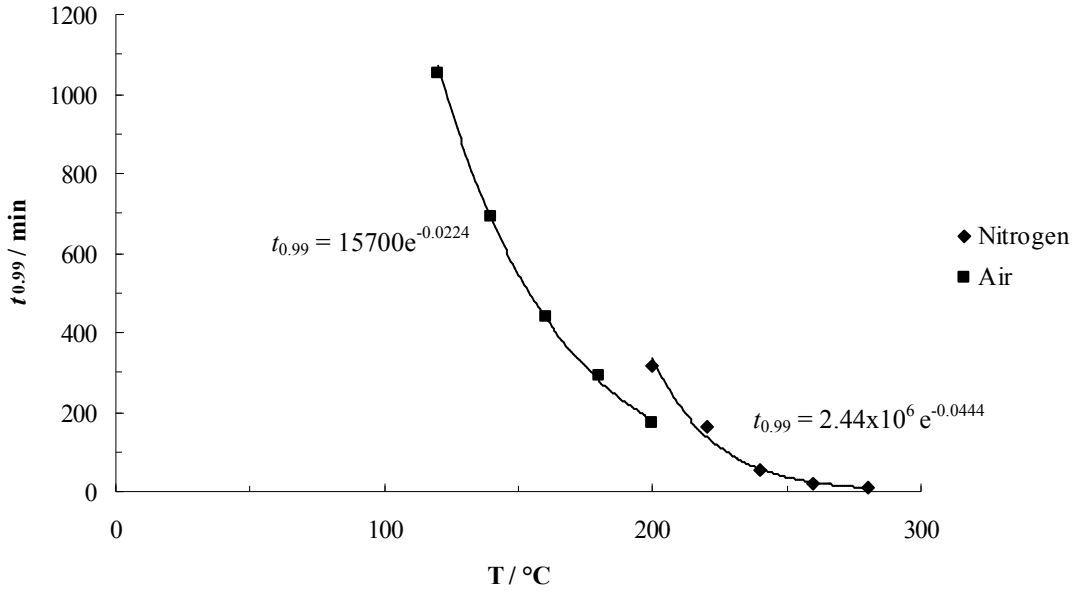


Figure 5.24 – $t_{0.99}$ versus isothermal temperature for [$C_3(NBu_2)_3$]TFSA under nitrogen and air atmospheres

Table 5-12 – Temperature for 1% decomposition over 10 h

	$T_{0.01/10}$ / °C	
	N_2	Air
$[C_3(NBu_2)_3]$TFSA	187	145
$[p_{1,4}]$TFSA	271	
$[C_2MIM]$TFSA	251	234
$[C_3(NBu_2)_3]$DCA	132	
$[p_{1,4}]$DCA	170	
$[C_3(NBu_2)_3]$Cl	110	

The T_d values, taken from TGA experiments where the temperature is ramped up at a constant rate, suggested triaminocyclopropenium salts were more stable than other cation classes with smaller, more coordinating anions, however, the $T_{0.01/10}$ values, taken from isothermal experiments, do not agree with this. For example, $[C_3(NBu_2)_3]$DCA has a $T_{0.01/10}$ of 132 °C, whereas for $[p_{1,4}]$DCA it is 170 °C despite $[p_{1,4}]$DCA having a lower T_d. This discrepancy might be caused by the triaminocyclopropenium cation's decomposition starting at a lower temperature, but the decomposition being less accelerated by a higher temperature than with other cations. The ramped TGA experiments will not show this initial, slow decomposition in the T_d value.

5.7.2 Chemical stability

If ionic liquids are going to be applied in chemical processes, an understanding of the chemical stability of the ionic liquid is needed.[42] For this reason, samples of triaminocyclopropenium salts were treated under various conditions to assess the stability of the cation. If the cation is not stable under those conditions, it is unlikely that it would be the best choice for a reaction under similar conditions as the solvent would not be recyclable. The chemical stability tests are based on those carried out by Afonso *et al.*[21,43] Small samples (250 mg) of $[C_3(NEt_2)_3]$Cl, $[C_3(NEt_2)_3]$DCA and $[C_3(NEt_2)_3]$TFSA were mixed with an equimolar amount of reagent (2 equivalents in the case of NH_3), and stirred at ambient temperature or heated to 60 °C. After 24 hours, ^{1}H-NMR was used to assess whether any degradation of the triaminocyclopropenium cation had occurred. The chemicals used were aqueous HCl (acid), aqueous NH_3 (weak base and nucleophile),

KOH (strong base), $NaBH_4$ (reducing agent), $NaIO_4$ (weak oxidising agent) and EtMgI (a Grignard reagent). The samples were also heated at 100 and 150 °C for 24 hours while exposed to an open atmosphere.

Table 5-13 – Chemical stability tests

		$[C_3(NEt_2)_3]Cl$		$[C_3(NEt_2)_3]DCA$		$[C_3(NEt_2)_3]TFSA$	
	Equiv	RT	60 °C	RT	60 °C	RT	60 °C
HCl (38%, aq)	1	[+]	[+]	[+]	[+]	[+]	[+]
NH_3(40%, aq)	2	[+]	[+]	[+]	[+]	[+]	[+]
KOH	1	[-]	[-]	[-]	[-]	[+]	[-]
$NaBH_4$	1	[+]	[+]	[+]	[+]	[+]	[+]
$NaIO_4$	1	[+]	[+]	[+]	[+]	[+]	[+]
EtMgI	1	[+]	[+]	[+]	[+]	[+]	[+]
		100 °C	150 °C	100 °C	150 °C	100 °C	150 °C
Air		[+]	[+]	[+]	[+]	[+]	[+]

Note: [+]: no change in ^{1}H-NMR, [-] degradation of $[C_3(NEt_2)_3]^+$ observed

The results of the chemical stability tests (Table 5-13) show that triaminocyclopropenium cations have very good chemical stability. Under acidic, weakly-basic, weakly-nucleophilic, reducing and weakly-oxidising conditions, no degradation of $[C_3(NEt_2)_3]^+$ was observed at both ambient temperature and 60 °C. This suggests that reactions that occur under those conditions can be carried out in triaminocyclopropenium ionic liquid solvents. When KOH was added, degradation of $[C_3(NEt_2)_3]^+$ to bis(diethylamino)cyclopropenone, diethylamine and other degradation products occurs, for $[C_3(NEt_2)_3]$TFSA at ambient temperature in which KOH did not appear to be soluble. It is important to note that the degradation of the cation is due to the nucleophilic nature of hydroxide, rather than any acidic nature of the triaminocyclopropenium cation.

In the stability tests, which are similar to the thermal decomposition experiments in air discussed previously, samples were heated in air at 100 and 150 °C and no decomposition or dramatic weight loss was observed. It should be noted that if decomposition had occurred, the decomposition products may not have been observed in the ^{1}H-NMR as these can get lost to the atmosphere, although weight loss would have been seen.

In the case of EtMgI, no degradation of the ionic liquid was observed, however, the Grignard reagent was not stable in the ionic liquids used and may have decomposed before reaction with the ionic liquid would take place. In order to test this further, a reaction between EtMgBr and CO_2, which should react to make propanoate, was carried out in $[C_3(NEt_2)_3]$TFSA. However, no products were detected, confirming the EtMgBr was not active in the ionic liquid. This instability of the Grignard reagent is probably due the lack of electron donating species that usually stabilize Grignard reagents, which is why they are generally prepared in THF or diethyl ether solutions. The anion could play this role, but these are in a low concentration and suspected to be less aggregated than in other ILs.

Tetraalkylphosphonium ionic liquids have been investigated as solvents for Grignard reactions,[44-46] and using the Grignard reagent PhMgBr, more diphenyl was formed in the neat ionic liquid reaction than when THF was also present as a cosolvent. This was due to shifting the Schlenk equilibrium between RMgX and R_2Mg and MgX_2. Introducing ether functionality to the alkyl chains was seen to stabilize the Grignard reagent. Since the interactions in the triaminocyclopropenium ionic liquids used were weaker (and thus not stabilizing) the Schlenk equilibrium may have been shifted.

5.7.3 Electrochemical stability

The electrochemical stability of an ionic liquid is another important property for any electrochemical application. It is the range of voltage over which the ionic liquid is electrochemically inert, i.e. neither oxidized nor reduced.[3] The upper limit is the resistance of the ionic liquid to oxidation, and is generally determined by the more electron rich species: the anion. The lower limit is the resistance of the ionic liquid to reduction, and is generally determined by the more electron poor species: the cation. The difference between these limits is the electrochemical window.

Cyclic voltammetry was carried out on a recrystallized sample of $[C_3(NEt_2)_3]$TFSA. A recrystallized sample was used as this has less impurities, which often have a negative impact on the cyclic voltammoogram. This was dried under vacuum at 50 °C for 72 hours

beforehand, due to water also having a negative effect[47,48] on the size of the electrochemical window and the introduction of reduction peaks associated with the water. The water content was 71 ppm.

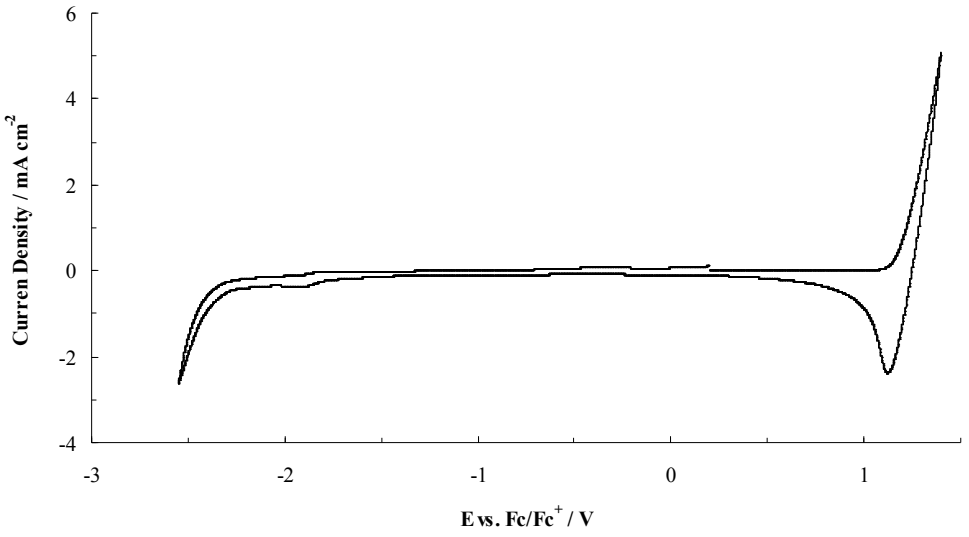


Figure 5.25 – Cyclic voltammogram of $[C_3(NEt_2)_3]$TFSA

The cyclic voltammogram is shown in Figure 5.25, measured with a platinum working electrode and referenced to the ferrocene/ferrocenium redox couple. If a cut-off limit for current density of 1 mA cm^{-2} is used, then the oxidation limit of $[C_3(NEt_2)_3]$TFSA is 1.2 V. Because oxidation involves the loss of electrons it is usually ascribed to the anion,[49] a more electron rich species. However, it is seen that the TFSA anion often resists oxidation up to +2.5 V, so in this case we are seeing oxidation of the cation. This measurement correlates well with that seen by Johnson,[50] who observed oxidation of $[C_3(NMe_2)_3]^+$ in acetonitrile at +1.3V. This low oxidation limit further reinforces the electron rich nature of the triaminocyclopropenium cation, due to the extensive π donation from the amino substituents. The oxidation limit is lower than all the other common cation classes, Table 5-14. Comparison of $[C_3(NEt_2)_3]$TFSA with $[C_4MIM]$TFSA shows the oxidation limit is 0.6 V lower, whereas against $[P_{14,6,6,6}]$TFSA it is 1.3V lower.

The reduction limit of $[C_3(NEt_2)_3]$TFSA was found to be –2.4 V. Reduction is usually ascribed to the cation, and this is the case here as well, as some TFSA ionic liquids have been observed to have a reduction limit of greater than –3.0 V. It is noted that Johnson[50] observed reduction of $[C_3(NMe_2)_3]^+$ at greater than –3.0 V, however, that was in solution. When comparisons are made to other classes of cations with TFSA anions, the reduction limit of $[C_3(NEt_2)_3]$TFSA is higher than [bpy]TFSA by 1.0 V and comparable to that of $[P_{14,6,6,6}]$, $[C_4MIM]$ and $[N_{6,2,2,2}]$TFSA.

The oxidation and reduction limits mean $[C_3(NEt_2)_3]$TFSA has a moderate electrochemical window of 3.6 V, due to the low oxidation of triaminocyclopropenium cations to the dication radical. The electrochemical window is smaller than imidazolium, phosphonium and ammonium ionic liquids, but comparable to pyridinium ionic liquids, which have a low reduction limit of pyridinium cations.

Table 5-14 – Comparison of reduction and oxidation potentials of TFSA salts

	$E_{(red)}$ V vs Fc/Fc^+	$E_{(ox)}$ V vs Fc/Fc^+	EW V
$[C_3(NEt_2)_3]^+$	–2.4	1.2	3.6
$[P_{14,6,6,6}]^{+a}$	–2.7	2.5	5.2
$[C_4MIM]^{+a}$	–2.5	1.8	4.3
$[N_{6,2,2,2}]^{+a}$	–2.6	2.1	4.7
$[C_4py]^{+b}$	–1.4	2.4	3.8

Note: [a] Ref[47] [b] Ref[51]

5.8 Solubility and miscibility

Another property investigated is the interaction of triaminocyclopropenium ionic liquids with a range of common solvents. This is especially relevant for the application of ionic liquids to chemical processes when the ionic liquid comes into contact with other solvents. Miscibility is the issue of whether two solvents will mix and form a single phase or an immiscible layer. Solubility is the issue of whether one compound will dissolve into another. Liquids that are miscible are then of course soluble, but liquids that are soluble are not necessarily miscible.

The solubility and miscibility was examined for all triaminocyclopropenium ionic liquid samples, where enough ionic liquid was available. When the sample was solid, or not enough material was available, only the solubility of the ionic salt in the solvent was assessed. The results obtained are shown in Table 5-15 and Table 5-16. M stands for the salt being totally soluble and totally miscible over the range of solvent ratios measured. Those that exhibited partial miscibility but not full solubility are shown by a P or by a number. The number represents the miscibility percentage for that solvent in the particular triaminocyclopropenium ionic liquid, eg $[C_3(NEt_2)_2NHex_2]$DCA and hexane formed an immiscible layer that consists of 33% hexane and 67% $[C_3(NEt_2)_2NHex_2]$DCA. N stands for the salt being non-soluble and non-miscible with the solvent at the tested solvent ratios. For solid samples, or those without enough material, then only solubility was tested; shown by S if soluble, and this probably implies full miscibility for liquid samples. This is implied by the samples where miscibility was tested – all salts that were soluble in the solvent were also fully miscible with the solvent. The solvents used were water, ethanol, dichloromethane, ethyl acetate, diethyl ether, toluene, and hexane. These provide a broad range of solvent properties from polar protic to nonpolar solvents.

The solid samples with melting points of greater than 50 °C were separated (Table 5-16), due to these samples having a high lattice energy. Samples that have a high lattice energy will have lower solubility in all solvents, and the ability of the solvent to provide specific interactions to break interactions holding the crystal together will have a strong influence on whether or not a sample will be soluble.

Table 5-15 – Miscibility table, sorted by anion. M = totally miscible, N = non miscible, P or number = partially miscible, S = soluble

	T_m °C	M_{cation} g mol^{-1}	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	n-Hexane
$[C_3(NAllyl_2)_3]Cl$		324	M	M	M	M	N	M	N
$[C_3(NBu_2)_3]Cl$		420	S	S	S	S	P	S	N
$[C_3(NPent_2)_3]Cl$		504	N	M	M	M	M	M	N
$[C_3(NHex_2)_3]Cl$		588	N	M	M	M	M	M	67
$[C_3(NDec_2)_3]Cl$	33	924	N	M	M	M	M	M	M
$[C_3(NEt_2)_3]NO_3$	–31	252	M	M	M	M	N	44	N
$[C_3(NBuMe)_3]NO_3$	24	294	M	M	M	M	38	67	N
$[C_3(NPr_2)_3]NO_3$		336	S	S	S	S	P	P	N
$[C_3(NBu_2)_3]NO_3$		420	9	M	M	M	67	M	33
$[C_3(NEt_2)_3]SCN$	–3	252	M	M	M	M	N	50	N
$[C_3(NBuMe)_3]SCN$		294	9	M	M	M	38		N
$[C_3(NEt_2)_2NMe_2]DCA$	32	224	M	M	M	M	N	N	N
$[C_3(NEt_2)_3]DCA$	10	252	41	M	M	M	50	50	N
$[C_3(NEt_2)_2NBuMe]DCA$	8	266	33	M	M	M	50	50	N
$[C_3(NBuMe)_3]DCA$		294	9	M	M	M	50	50	N
$[C_3(NEt_2)_2NHexMe]DCA$		294	23	M	M	M	50	67	23
$[C_3(NEt_2)_2NBu_2]DCA$	30	308	N	M	M	M	33	50	N
$[C_3(NAllyl_2)_3]DCA$	24	324	9	M	M	M	50	50	N
$[C_3(NPr_2)_3]DCA$	49	336	P	S	S	S	N	P	N
$[C_3(NEt_2)_2NHex_2]DCA$		364	N	M	M	M	50	M	33
$[C_3(NBu_2)_3]DCA$	14	420	N	M	M	M	50	M	41
$[C_3(NPent_2)_3]DCA$		504	N	M	M	M	M	M	41

	T_m °C	M_{cation} g mol^{-1}	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	n-Hexane
$[C_3(NHex_2)_3]DCA$		588	N	M	M	M	M	M	50
$[C_3(NDec_2)_3]DCA$	–13	924	N	M	M	M	M	M	M
$[C_3(NBu_2)_3]OTf$	42	420	N	M	M	M	M	M	N
$[C_3(NEt_2)_3]ClO_4$	39	252	P	S	S	S	N	S	N
$[C_3(NEt_2)_3]BF_4$	24	252	N	M	M	M	N	50	N
$[C_3(NBuMe)_3]BF_4$		294	N	M	M	M	N	67	N
$[C_3(NBu_2)_3]BF_4$	29	420	N	S	S	S	P	S	P
$[C_3(NEt_2)_2NMe_2]TFSA$	17	224	N	M	M	M	50	50	N
$[C_3(NEt_2)_3]TFSA$	19	252	N	M	M	M	N	50	N
$[C_3(NEt_2)_2NBuMe]TFSA$		266	N	M	M	M	50	50	N
$[C_3(NEt_2)_2NHexH]TFSA$		280	N	M	M	M	M	67	N
$[C_3(NBuMe)_3]TFSA$		294	N	M	M	M	M	67	N
$[C_3(NEt_2)_2NHexMe]TFSA$		294	N	M	M	M	67	50	23
$[C_3(NEt_2)_2NBu_2]TFSA$	–4	308	N	M	M	M	67	50	23
$[C_3(NAllyl_2)_3]TFSA$	9	324	N	M	M	M	M	75	17
$[C_3(NPr_2)_3]TFSA$	30	336	N	M	M	M	67	50	N
$[C_3(NEt_2)_2NHex_2]TFSA$		364	N	M	M	M	M	67	33
$[C_3(NBu_2)_3]TFSA$	3	420	N	M	M	M	M	M	33
$[C_3(NPent_2)_3]TFSA$	4	504	N	M	M	M	M	M	44
$[C_3(NHex_2)_3]TFSA$	3	588	N	M	M	M	M	M	67
$[C_3(NDec_2)_3]TFSA$	8	924	N	M	M	M	M	M	M
$[C_3(NHex_2)_3]DBP$		588	N	M	M	M	M	M	M

Table 5-16 – Solubility of salts with melting points over 50 °C

	T_m °C	M_{cation} g mol^{-1}	H_2O	EtOH	CH_2Cl_2	EtOAc	Et_2O	Toluene	n-Hexane
$[C_3(NEt_2)_3]Cl$	92	252	S	S	S	N	N	N	N
$[C_3(NBuMe)_3]Cl$	80	294	S	S	S	S	N	S	N
$[C_3(NPr_2)_3]Cl$	75	336	S	S	S	N	N	N	N
$[C_3(N^iPr_2)_2NBu_2]Cl$	119	364	S	S	S	N	N	N	N
$[C_3(NC_{18}Me)_3]Cl$	52	882	Swelled	S	S	N	N	N	N
$[C_3(NEt_2)_2N(CH_2CH_2OH)_2]DCA$	80	284	M	S	S	N	N	N	N
$[C_3(NC_{18}Me)_3]DCA$	52	882	N	N	S	N	N	N	N
$[C_3(NPr_2)_3]BF_4$	77	336	N	N	S	N	N	N	N
$[C_3(NMe_2)_3]TFSA$	105	168	N	N	S	S	N	P	N
$[C_3(NC_{18}Me)_3]TFSA$	64	882	N	N	S	N	N	S	N

The two main factors that influence solubility and miscibility are the anion and the size of the cation, there is also a minor influence from the symmetry of the cation. The anions used here range from the very hydrophilic chloride, to the very hydrophobic TFSA. Those which are more hydrophilic will favour the polar solvents such as water whereas those that are more hydrophobic will favour the nonpolar salt. The order of anions from hydrophilic to hydrophobic observed here is Cl > NO_3, SCN > DCA > OTf, ClO_4 > BF_4, TFSA. Due to the influence of the anion Table 5-15 was sorted by anion, so cation effects can more clearly be seen. It is important to remember that it is not just polarity of the anion that affects solubility and miscibility, but specific interactions such as hydrogen bonds also play a role. For example, DCA salts have higher solubility in toluene than in diethyl ether despite the similar polarities of the solvents. This is due to π interactions that can occur with the aromatic toluene. DCA is also a better hydrogen bond acceptor, so has increased solubility with water.

The second major influence is the size of the triaminocyclopropenium cation. As the total alkyl chain length increases, more van der Waal forces are present and the ionic regions are diluted, which shifts solubility away from polar solvents towards less polar solvents. This can be seen to be generally true in the chloride, nitrate, DCA and TFSA anion series. For example, the smallest DCA salt is $[C_3(NEt_2)_2NMe_2]$DCA and is totally miscible in water and totally with immiscible in diethyl ether, toluene and hexane. As the cation size is increased, water solubility decreases, until it becomes insoluble at all measured solvent ratios. The opposite is observed for the non polar solvents, diethyl ether, toluene and hexane, which first become partially miscible (soluble), then fully miscible for the very large cation $[C_3(NDec_2)_3]^+$. With the TFSA and DCA D_{3h} symmetry series with only saturated alkyl chains, the only measurement that does not fit the trend of longer alkyl chains favouring the less polar solvents is that of $[C_3(NPr_2)_3]$DCA in diethyl ether. This sample was insoluble and did not form an immiscible liquid layer, whereas $[C_3(NEt_2)_3]$DCA and $[C_3(NBu_2)_3]$DCA both formed immiscible liquids, This can be explained by the higher lattice energy of $[C_3(NPr_2)_3]$DCA causing lower solubility.

There is a minor influence on solubility due to the symmetry of the cation, although this is much weaker than the anion or size effects. For similarly sized cations, the less symmetric cations will have one or more longer alkyl chains compared to the more symmetric cation. This longer alkyl chain has the effect of shifting solubility towards less polar solvents, which outweighs the less symmetric molecule's increased dipole. For example, $[C_3(NEt_2)_2NBu_2]$TFSA and $[C_3(NEt_2)_2NHexMe]$TFSA both show partial miscibility with hexane while the larger $[C_3(NPr_2)_3]$TFSA does not show any solubility of hexane. It is also noted that as the symmetry of the cation is reduced, the lattice energy of the solid phase will decrease, and as discussed previously high lattice energies will decrease solubilities.

As with the anion, specific interactions originating on the cation can also contribute towards solubility. There are two cases of this seen with the cations used; $[C_3(NAllyl_2)_3]$TFSA and $[C_3(NEt_2)_2NHexH]^+$. In the case of $[C_3(NAllyl_2)_3]$TFSA, it is totally miscible with diethyl ether, and partially miscible with toluene and hexane, whereas the similarly sized $[C_3(NPr_2)_3]$TFSA is only partially miscible with diethyl ether, has less solubility of toluene, and hexane is not soluble in the ionic liquid. The alkene functional groups allow for greater interaction, and therefore solubility, than alkyl chains that only have van der Waals interactions. When $[C_3(NEt_2)_2NHexH]$TFSA is compared to the similarily sized $[C_3(NEt_2)_2NHexMe]$TFSA differences are also seen due to a methyl group being replaced with a proton. $[C_3(NEt_2)_2NHexH]$TFSA shows total miscibility with diethyl ether, partial miscibility with toluene and total immiscibility with hexane, whereas $[C_3(NEt_2)_2NHexMe]$TFSA shows partial miscibility with all three solvents. In the case of diethyl ether, a proton on the nitrogen can hydrogen bond to the oxygen of diethyl ether, while a methyl group has much less interaction. However, when hexane is used no hydrogen bonds are possible with the organic solvent, only with other $[C_3(NEt_2)_2NHexH]^+$ cations, which would be broken if hexane were to dissolve into the ionic liquid layer.

While testing the solubility of $[C_3(NC_{18}Me)_3]$Cl in water, it was noted that the solid sample swelled, with the 100 mg sample increasing to a volume of approximately 2 mL

of a wet gel-type substance. The original solid sample could be regenerated by heating under vacuum. This is thought to be due to water hydrogen bonding to the chloride anion, and long alkyl chains that can allow for large cavities in which the hydrated chloride can fill.

5.9 Crystal structures

During the course of this work, three crystal structures were obtained. While there was no concerted effort to grow crystals, several salts formed crystals that were of adequate quality for single crystal x-ray crystallography. These samples were the $[C_3(NMe_2)_3]$TFSA, $[C_3(NPr_2)_3]$TFSA and $[C_3(NPr_2)_3]$DCA salts. All three samples are quite hydrophobic and have melting points above ambient temperature, factors which helped crystal growth. Whereas the melting point of $[C_3(NMe_2)_3]$TFSA is 105 °C, the melting points of $[C_3(NPr_2)_3]$TFSA and DCA are much lower, 30 and 59 °C, respectively. As was discussed in the DSC section earlier in this chapter, $[C_3(NMe_2)_3]^+$ and $[C_3(NPr_2)_3]^+$ have melting points higher than other D_{3h} symmetry cations or similarly sized cations with less symmetry, meaning that melting points for those compounds are below ambient temperature.

In terms of the bond lengths and angles (Table 5-17, Table 5-18 and Table 5-19), the central triaminocyclopropenium core is very close to being symmetric, with bond lengths and angles similar in all compounds. Bond lengths and angles are similar to those found in structures from the literature,[52-58] and can be rationalized for the same reasons, as discussed in the introductory chapter. The C-C bonds are 1.38 Å, short due to the bent sigma bonds. The C-N exocyclic bonds are 1.33 Å, also short due to π donation from the nitrogen, placing the length in between C-N single and double bonds. The nitrogen to alkyl chain α-carbon is also slightly short, due to the partial positive charge delocalization on to the nitrogen. In terms of the angles, the internal angles are very close to 60° with the exocyclic C-N bond at 150°, although the internal angle will be increased by the bent bonds, which is not observable by this technique. The nitrogen atoms are all trigonal planar with angles very close to 120° and with the sum of the angles around each nitrogen being at least 356°. This planarity is due to sp^2 hybridization, caused by the π

donation into the cyclopropenium ring. The planar nitrogen is coplanar with the cyclopropenium ring, which results in a planar core. In the cases of $[C_3(NPr_2)_3]$TFSA and DCA, the six propyl side chains surrounding this central core are out of this plane.

Table 5-17 – Selected bond lengths for $[C_3(NPr_2)_3]$TFSA, for each cation in the asymmetric unit

	Length/Å	Length/Å		Angle/°	Angle/°
C1-C2	1.377	1.381	C1-C2-C3	60.4	59.8
C1-C3	1.385	1.379	C2-C1-C3	59.7	60.1
C2-C3	1.376	1.382	C1-C3-C2	59.8	60.0
C1-N1	1.316	1.324	N1-C1-C2	150.7	149.2
C2-N2	1.332	1.329	N1-C1-C3	149.5	150.6
C3-N3	1.330	1.324	N2-C2-C1	151.6	148.4
N1-C11a	1.461	1.468	N2-C2-C3	147.9	151.6
N1-C12a	1.461	1.463	N3-C3-C1	150.1	149.8
N2-C21a	1.462	1.453	N3-C3-C2	150.0	150.0
N2-C22a	1.457	1.463	C1-N1-C11a	120.1	121.0
N3-C31a	1.459	1.469	C1-N1-C12a	120.1	121.2
N3-C32a	1.464	1.481	C12a-N1-C11a	119.1	117.2
			C2-N2-C21a	121.4	119.4
			C2-N2-C22a	119.1	121.7
			C21a-N2-C22a	117.2	117.7
			C3-N3-C31a	120.0	119.6
			C3-N3-C32a	120.8	120.5
			C31a-N3-C32a	119.0	119.0

Table 5-18 – Selected bond lengths and angles for $[C_3(NPr_2)_3]$DCA, extra measurements due to the disordered propyl side chain

	Length/Å	Length/Å		Angle/°	Angle/°
C1-C2	1.380		C1-C2-C3	59.8	
C1-C3	1.374		C2-C1-C3	59.9	
C2-C3	1.375		C1-C3-C2	60.2	
C1-N1	1.330		N1-C1-C2	149.9	
C2-N2	1.329		N1-C1-C3	150.0	
C3-N3	1.327		N2-C2-C1	150.2	
N1-C11a	1.470		N2-C2-C3	149.8	
N1-C12a	1.465		N3-C3-C1	150.0	
N2-C21a	1.467		N3-C3-C2	149.7	
N2-C22a	1.464		C1-N1-C11a	120.5	
N3-C31a	1.476		C1-N1-C12a	120.5	
N3-C32a	1.496	1.539	C12a-N1-C11a	118.3	
			C2-N2-C21a	120.7	
			C2-N2-C22a	120.9	
			C21a-N2-C22a	117.9	
			C3-N3-C31a	119.5	
			C3-N3-C32a	118.3	122.9
			C31a-N3-C32a	118.8	113.6

Table 5-19 – Selected bond lengths for $[C_3(NMe_2)_3]$TFSA, for each cation in the asymmetric unit

	Length/Å	Length/Å	Length/Å		Angle/°	Angle/°	Angle/°
C1-C2	1.378	1.373	1.371	C1-C2-C3	60.2	59.9	60.1
C1-C3	1.381	1.377	1.377	C2-C1-C3	59.8	60.3	60.1
C2-C3	1.376	1.382	1.377	C1-C3-C2	59.9	59.9	59.7
C1-N10	1.327	1.326	1.326	N10-C1-C2	149.2	149.6	149.4
C2-N20	1.326	1.320	1.325	N10-C1-C3	150.9	149.9	150.3
C3-N30	1.327	1.321	1.322	N20-C2-C1	148.9	149.9	149.6
N10-C11	1.454	1.451	1.453	N20-C2-C3	150.8	150.0	150.2
N10-C12	1.456	1.447	1.448	N30-C3-C1	149.6	149.3	150.5
N20-C21	1.446	1.455	1.458	N30-C3-C2	150.2	151.0	149.6
N20-C22	1.448	1.447	1.455	C1-N10-C11	118.7	118.6	121.6
N30-C31	1.453	1.449	1.454	C1-N10-C12	120.0	119.5	120.4
N30-C32	1.457	1.448	1.453	C12-N10-C11	117.8	121.1	117.7
				C2-N20-C21	119.8	118.9	119.8
				C2-N20-C22	121.1	119.7	120.8
				C21-N20-C22	119.0	121.2	119.1
				C3-N30-C31	119.5	121.3	121.1
				C3-N30-C32	120.0	119.9	120.6
				C31-N30-C32	117.3	118.4	117.7

The unit cell of $[C_3(NPr_2)_3]$TFSA is shown in Figure 5.26. The asymmetric unit contains two cations and anions, which have similar environments, bond lengths and angles, but their planes are 20° out of alignment. These show no strong specific interactions, due to the lack of any hydrogen bond donors, π systems other than the triaminocyclopropenium cation and a dispersed charge. In Figure 5.27, a single $[C_3(NPr_2)_3]^+$ cation is shown with two surrounding anions, one above and one below the ring, which each have an oxygen and fluorine atom roughly pointed towards the ring. While not shown in the figure, the other trifluoromethanesulfonyl branches of the TFSA anions are in position over other $[C_3(NPr_2)_3]^+$ cations. With each cation and anion being associated with two of the opposite ion, there is no strong ion pairing occurring. The sterically awkward TFSA anion was present in the trans configuration, which is the lowerest energy conformation.[59]

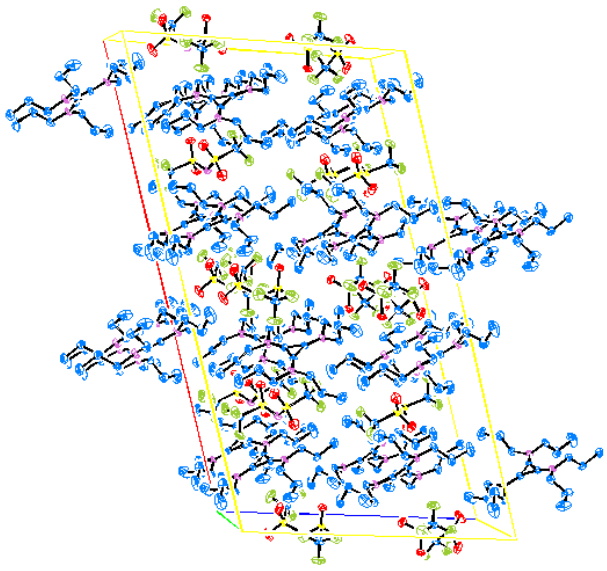


Figure 5.26 – Unit cell of $[C_3(NPr_2)_3]$TFSA structure

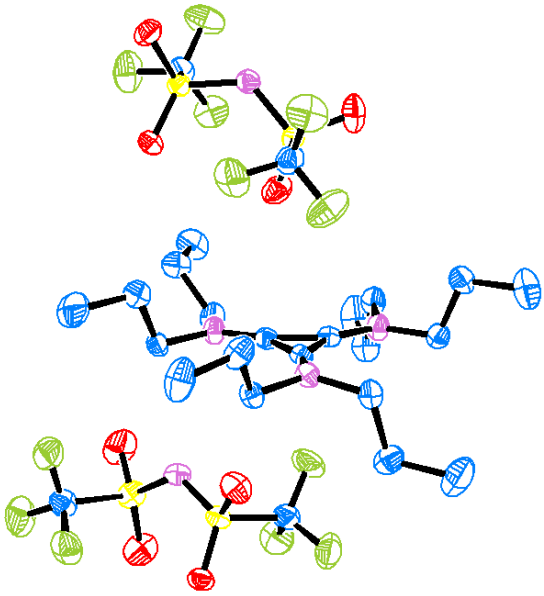


Figure 5.27 – ORTEP of $[C_3(NPr_2)_3]^+$ cation with two surrounding TFSA anions. Thermal ellipsoids are drawn at 50% probability, with hydrogen atoms omitted.

The unit cell of $[C_3(NPr_2)_3]$DCA is shown in Figure 5.28. The asymmetric unit is one anion and one cation. Figure 5.29 shows the $[C_3(NPr_2)_3]^+$ cation, the DCA anion sitting above the triaminocyclopropenium ring and another partial cation with an alkyl chain filling in the shape below the triaminocyclopropenium ring. Due to the π systems on both the cation and anion, there are π interactions that cause the anion to sit directly over the ring, 5° from being on parallel planes. The association of one anion with one cation means the crystal has more ion pairing than the TFSA salt. These units stack with parallel planes of the anions and cations to form a layer, with the interface to the neighbouring layer, which has its planes at 45° to the first, being propyl side chains. In Figure 5.28 the layers are vertically perpendicular to the plane of the page.

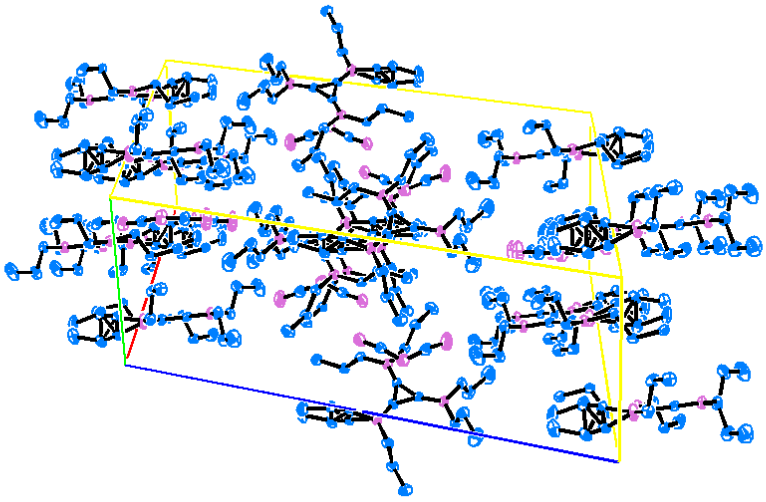


Figure 5.28 – Unit cell of $[C_3(NPr_2)_3]$DCA structure

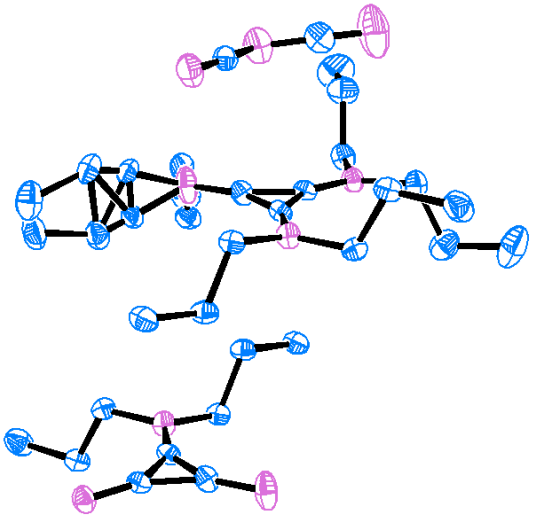


Figure 5.29 – ORTEP of $[C_3(NPr_2)_3]^+$ cation with neighbouring DCA anion and $[C_3(NPr_2)_3]^+$ cation. Thermal ellipsoids are drawn at 50% probability, with hydrogen atoms omitted.

The unit cell of $[C_3(NMe_2)_3]$TFSA is shown in Figure 5.30. The asymmetric unit contains three cations and anions, which have similar environments, bond lengths and angles, with their planes only 5° out of alignment. The asymmetric unit cell is shown in Figure 5.31. With the cations nearly being co-planar and the ions are of similar size, these form columns of alternating anions and cations. With each cation and anion being associated

with two of the opposite, there is no strong ion pairing occurring. The sterically awkward TFSA anion was present in the trans configuration, which is the lowerest energy conformation.[59,60]

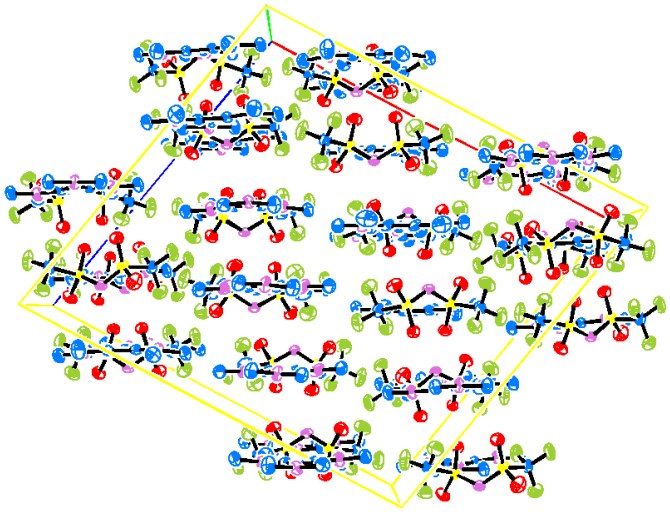


Figure 5.30– Unit cell of $[C_3(NMe_2)_3]$TFSA structure

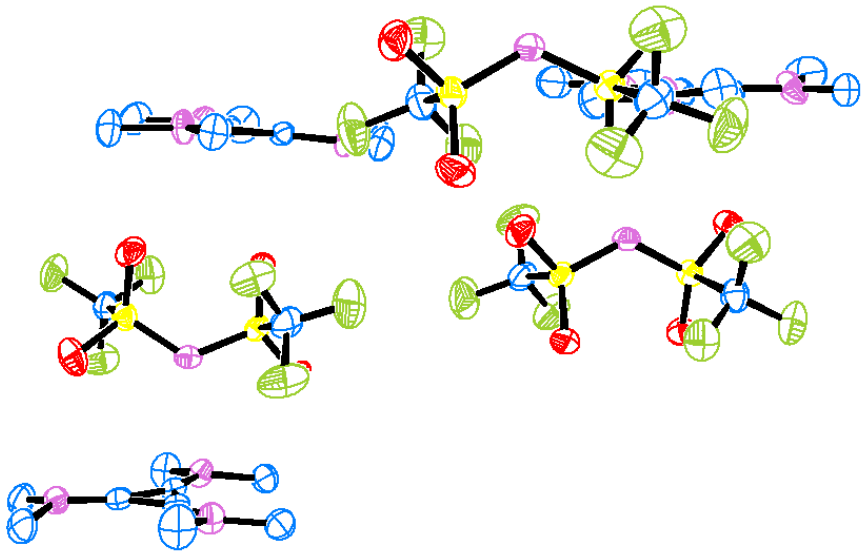


Figure 5.31 – ORTEP of $[C_3(NMe_2)_3]$TFSA asymmetric cell. Thermal ellipsoids are drawn at 50% probability, with hydrogen atoms omitted.

5.10 Conclusions

A number of properties of triaminocyclopropenium ionic liquids have been investigated. DSC of triaminocyclopropenium salts found glass transitions, solid-solid transitions and melting points. A range of melting points have been observed, from –26 to 126 °C, with the vast majority of salts having melting points of less than 100 °C, thus qualifying them as ionic liquids. More than half of the salts investigated are liquid at room temperature.

The densities of triaminocyclopropenium ionic liquids were observed to be slightly lower than other ionic liquids, from 0.890 to 1.277 g mol^{-1}, at 20 °C. This is due to the higher molecular weight of the cations. The densities were mostly anion dependent, with heavier anions generally resulting in higher densities, although density also showed some dependency on the size of the cation, with larger cations resulting in lower densities.

The viscosities of triaminocyclopropenium ionic liquids ranged from 58.4 to 554 mPa s, at 20 °C. The viscosities were anion dependent and also had a large dependence on the size of cation, with larger cations resulting in higher viscosities. Other classes of ionic liquids have lower viscosities than the triaminocyclopropenium ionic liquids reported here, however, triaminocyclopropenium ionic liquids are less viscous if compared to similarly-sized cations of other classes.

The conductivity of triaminocyclopropenium ionic liquids ranged from 0.02 to 4.69 mS cm^{-1} at 20 °C. While the molar conductivity of triaminocyclopropenium ionic liquids is good, the generally larger size of the cation results in lower ion concentrations, which lowers the conductivity compared to other classes of cations.

Triaminocyclopropenium ionic liquids show good ionicity, all ionic liquids reported here are less than one order of magnitude below the ideal line on a Walden plot. Very large triaminocyclopropenium cations started to show decreasing ionicity, due to entrapment of the much smaller anion causing increased ion pairing. Diffusion measurements on $[C_3(NBu_2)_3]$TFSA showed ΔI is 0.10 for this ionic liquid, confirming a high ionicity. This is probably due to the electron-rich nature the cation.

The thermal stabilities of triaminocyclopropenium salts are good, and are comparable to other classes of ionic liquids. Onset temperatures at 10 °C min^{-1} were in the range 339 to 413 °C for TFSA salts, however, lower with anions such as chloride or DCA and lower with allyl or hydroxyl substituents. The long term thermal stability of $[C_3(NBu_2)_3]$TFSA was lower than $[C_2MIM]$TFSA, however, it was still reasonable.

Triaminocyclopropenium ionic liquids showed no decomposition in acidic, weakly-basic, weakly-nucleophilic, reducing and weakly-oxidising environment. However, under strongly basic conditions (OH^-) bis(dialkylamino)cyclopropenone is formed.

The electrochemical window of $[C_3(NEt_2)_3]$TFSA was 3.6 V, between –2.4 and +1.2 V. The oxidation limit is low due to the electron rich nature of the triaminocyclopropenium cation. The reduction limit is good and comparable to other classes of ionic liquids.

Triaminocyclopropenium ionic liquids showed a full range of solubility and miscibility. Depending on the anion and the size and interactions of the cation, the triaminocyclopropenium ionic liquids ranged from fully miscible with polar, protic water to fully miscible with non-polar, aprotic hexane.

Crystal structures of $[C_3(NPr_2)_3]$TFSA, $[C_3(NPr_2)_3]$DCA and $[C_3(NMe_2)_3]$TFSA were solved and reported.

5.11 References

(1) Appetecchi, G. B.; Montanino, M.; Zane, D.; Carewska, M.; Alessandrini, F.; Passerini, S. *Electrochimica Acta* **2009**, *54*, 1325-1332.

(2) Erdmenger, T.; Vitz, J.; Wiesbrock, F.; Schubert, U. S. *J. Mater. Chem.* **2008**, *18*, 5267-5273.

(3) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH, **2008**.

(4) Holbrey, J. D.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1999**, 2133-2139.

(5) Adamova, G.; Gardas, R. L.; Rebelo, L. P. N.; Robertson, A. J.; Seddon, K. R. *Dalton Trans.* **2011**, *40*, 12750-12764.

(6) Tokuda, H.; Tsuzuki, S.; Susan, M. A. B. H.; Hayamizu, K.; Watanabe, M. *J. Phys. Chem. B* **2006**, *110*, 19593-19600.

(7) Fredlake, C. P.; Crosthwaite, J. M.; Hert, D. G.; Aki, S. N. V. K.; Brennecke, J. F. *J. Chem. Eng. Data* **2004**, *49*, 954-964.

(8) Pringle, J. M.; Golding, J.; Forsyth, C. M.; Deacon, G. B.; Forsyth, M.; MacFarlane, D. R. *J. Mater. Chem.* **2002**, *12*, 3475-3480.

(9) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. *Green Chem.* **2001**, *3*, 156-164.

(10) Endres, F.; MacFarlane, D.; Abbott, A. *Electrodeposition from ionic liquids*; Wiley-VCH, **2008**.

(11) Pringle, J. M.; Howlett, P. C.; MacFarlane, D. R.; Forsyth, M. *J. Mater. Chem.* **2010**, *20*, 2056-2062.

(12) MacFarlane, D. R.; Meakin, P.; Amini, N.; Forsyth, M. *J. Phys. Condens. Matter* **2001**, *13*, 8257-8267.

(13) Belieres, J. P.; Angell, C. A. *J. Phys. Chem. B* **2007**, *111*, 4926-4937.

(14) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. *J. Phys. Chem. B* **2004**, *108*, 16593-16600.

(15) Tokuda, H.; Ishii, K.; Susan, M. A. B. H.; Tsuzuki, S.; Hayamizu, K.; Watanabe, M. *J. Phys. Chem. B* **2006**, *110*, 2833-2839.

(16) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. *J. Phys. Chem. B* **2005**, *109*, 6103-6110.

(17) Seddon, K. R.; Stark, A.; Torres, M.-J. In *Clean solvents: alternative media for chemical reactions and processing*; American Chemical Society, **2002**.

(18) Fitchett, B. D.; Knepp, T. N.; Conboy, J. C. *J. Electrochem. Soc.* **2004**, *151*, E219-E225.

(19) Scheiner, C.; Zugmann, S.; Hartl, R.; Gores, H. J. *J. Chem. Eng. Data* **2010**, *55*, 1784-1788.

(20) Murray, S. M.; O'Brien, R. A.; Mattson, K. M.; Ceccarelli, C.; Sykora, R. E.; West, K. N.; James H. Davis, J. *Angew. Chem. Int. Ed.* **2010**, *49*, 2755-2758.

(21) Kulkarni, P. S.; Branco, L. C.; Crespo, J. G.; Nunes, M. C.; Raymundo, A.; Afonso, C. A. M. *Chem. Eur. J.* **2007**, *13*, 8478-8488.

(22) Sun, J.; Forsyth, M.; MacFarlane, D. R. *J. Phys. Chem. B* **1998**, *102*, 8858-8864.

(23) Tsunashima, K.; Sugiya, M. *Electrochem. Commun.* **2007**, *9*, 2353-2358.

(24) Kunkel, H.; Maas, G. *Eur. J. Org. Chem.* **2007**, 3746-3757.

(25) Abbott, A. P. *ChemPhysChem* **2004**, *5*, 1242-1246.

(26) Ediger, M. D.; Angell, C. A.; Nagel, S. R. *J. Phys. Chem.* **1996**, *100*, 13200-13212.

(27) Angell, C. A. *Molten Salts and Ionic lquids: Never the twain?* **2010**, 1-24.

(28) Angell, C. A. *J. Non-Cryst. Solids* **1991**, *131-133*, 13-31.

(29) MacFarlane, D. R.; Forsyth, M.; Izgorodina, E. I.; Abbott, A. P.; Annat, G.; Fraser, K. *Phys. Chem. Chem. Phys.* **2009**, *11*, 4962-4967.

(30) Ueno, K.; Zhao, Z.; Watanabe, M.; Angell, C. A. *J. Phys. Chem. B* **2012**, *116*, 63-70.

(31) Xu, W.; Cooper, E. I.; Angell, C. A. *J. Phys. Chem. B* **2003**, *107*, 6170-6178.

(32) Fraser, K. J.; Izgorodina, E. I.; Forsyth, M.; Scott, J. L.; MacFarlane, D. R. *Chem. Commun.* **2007**, 3817-3819.

(33) Armstrong, J. P.; Hurst, C.; Jones, R. G.; Licence, P.; Lovelock, K. R. J.; Satterley, C. J.; Villar-Garcia, I. J. *Phys. Chem. Chem. Phys.* **2007**, *9*, 982-990.

(34) Noda, A.; Hayamizu, K.; Watanabe, M. *J. Phys. Chem. B* **2001**, *105*, 4603-4610.

(35) Ueno, K.; Tokuda, H.; Watanabe, M. *Phys. Chem. Chem. Phys.* **2010**, *12*, 1649-1658.

(36) Kamavaram, V.; Reddy, R. G. *Int. J. Therm. Sci.* **2008**, *47*, 773-777.

(37) Sesto, R. E. D.; McCleskey, T. M.; Macomber, C.; Ott, K. C.; Koppisch, A. T.; Baker, G. A.; Burrell, A. K. *Thermochimica Acta* **2009**.

(38) Wooster, T. J.; Johanson, K. M.; Fraser, K. J.; MacFarlane, D. R.; Scott, J. L. *Green Chem.* **2006**, *8*, 691-696.

(39) Irran, E.; Jurgens, B.; Schnick, W. *Chem. Eur. J.* **2001**, *7*, 5372-5381.

(40) Crosthwaite, J. M.; Muldoon, M. J.; Dixon, J. K.; Anderson, J. L.; Brennecke, J. F. *J. Chem. Thermodyn.* **2005**, *37*, 559-568.

(41) Baranyai, K. J.; Deacon, G. B.; MacFarlane, D. R.; Pringle, J. M.; Scott, J. L. *Aust. J. Chem.* **2004**, *57*, 145-147.

(42) Sowmiah, S.; Srinivasadesikan, V.; Tseng, M.-C.; Chu, Y.-H. *Molecules 2009, 14, 3780-3813* **2009**, *14*, 3780-3813.

(43) Mateus, N. M. M.; Branco, L. C.; Lourenço, N. M. T.; Afonso, C. A. M. *Green Chem.* **2003**, *5*, 347-352.

(44) Ramnial, T.; Taylor, S. A.; Clyburne, J. A. C.; Walsby, C. J. *Chem. Commun.* **2007**, 2066-2068.

(45) Itoh, T.; Kude, K.; Hayase, S.; Kawatsura, M. *Tetrahedron Lett.* **2007**, *48*, 7774-7777.

(46) Ramnial, T.; Ino, D. D.; Clyburne, J. A. C. *Chem. Commun.* **2005**, 325-327.

(47) O'Mahony, A. M.; Silvester, D. S.; Aldous, L.; Hardacre, C.; Compton, R. G. *J. Chem. Eng. Data* **2008**, *53*, 2884-2891.

(48) Schroder, U.; Wadhawan, J. D.; Compton, R. G.; Marken, F.; Suarez, P. A. Z.; Consorti, C. S.; Souza, R. F. d.; Dupont, J. *New J. Chem.* **2000**, *24*, 1009-1015.

(49) Ohno, H. *Electrochemical Aspects of Ionic Liquids*; John Wiley & Sons, 2005.

(50) Johnson, R. W. *Tetrahedron Lett.* **1976**, *8*, 589-592.

(51) Matsumoto, H.; Yanagida, M.; Tanimoto, K.; Kojima, T.; Tamiya, Y.; Miyazaki, Y. *Proc. Electrochem. Soc.: Molten Salts XII* **2000**, 186.

(52) Butchard, J. R.; Curnow, O. J.; Pipal, R. J.; Robinson, W. T.; Shang, R. *J. Phys. Org. Chem.* **2008**, *21*, 127-135.

(53) Butchard, J. R.; Curnow, O. J.; Garrett, D. J.; Maclagan, R. G. A. R. *Angew. Chem. Int. Ed.* **2006**, *45*, 7550-7553.

(54) Schafer, H. N.; Burzlaff, H.; Grimmeiss, A. M. H.; Weiss, R. *Acta Cryst.* **1992**, *C48*, 912-913.

(55) Schafer, H. N.; Burzlaff, H.; Grimmeiss, A. M. H.; Weiss, R. *Acta Cryst.* **1992**, *C48*, 795-798.

(56) Schafer, H. N.; Burzlaff, H.; Grimmeiss, A. M. H.; Weiss, R. *Acta Cryst.* **1991**, *C47*, 1808-1811.

(57) Cowman, C. D.; Thibeault, J. C.; Ziolo, R. F.; Gray, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 3209-3214.

(58) Ku, A. T.; Sundaralingam, M. *J. Am. Chem. Soc.* **1972**, *94*, 1688-1692.

(59) Holbrey, J. D.; Reichert, W. M.; Rogers, R. D. *Dalton Trans.* **2004**, 2267-2271.

(60) Henderson, W. A.; Trulove, P. C.; DeLong, H. D.; Jr, V. G. Y. *ECS Transactions* **2003**, *3*, 83-88.

Chapter 6

6 Preliminary investigation of ionic liquid fluorides

Introduction

Parallel to the work on triaminocyclopropenium ionic liquids, a preliminary investigation of ionic liquids with fluoride anions have been carried out. Fluoride anions have the potential to make ionic liquids with interesting properties due to the reactivity of fluoride.[1,2] Fluoride salts, such as tetrabutylammonium fluoride (TBAF), have many uses as fluorinating reagents. The more "naked" (higher donor ability) the fluoride anion is, the higher the reactivity.[3] However, this reactivity causes difficulties with organic fluoride salts often being unstable due to the reactive fluoride[4] or insoluble in aprotic solvents. Ionic liquid fluorides could potentially be used to carry out fluorination reactions, if stable. It would also be interesting to see how ionic liquid fluorides interact with solutes: either gases,[5,6] liquids or solids.[2]

Triaminocyclopropenium cations were considered as counter ions to fluoride anions for two reasons: first, there are no acidic protons, and second, cyclopropenium compounds benefit from the greatest aromatic stability gain compared to other aromatic systems. Cations with acidic protons will easily be deprotonated by fluoride anions, which are basic and become a much stronger base as it becomes less solvated. This is predicted to occur in imidazolium fluoride salts: Ab Initio calculations on 1-ethyl-3-methylimidazolium fluoride show that covalent bonding between the fluorine atom and a proton extracted from the 2 position of the imdazolium cation is preferred over the ionic form, which gives HF and a stable Arduengo carbene.[2,7] Imidazolium-based ionic liquid fluorides have only been reported with solvated fluoride anions.[2,8] It was also thought triaminocyclopropenium cations might be more resistant to Hofmann elimination, which causes the decomposition of tetraalkylammonium fluorides. On the other hand, triaminocyclopropenium cations are sensitive to strong nucleophiles, such as hydroxide and possibly fluoride itself. For this reason, it was known that even if triaminocyclopropenium salts proved to be stable to fluoride, any kind of naked fluoride ionic liquid would be a moisture sensitive ionic liquid.

While initially interest was mainly directed towards synthesizing less solvated fluoride anions, so-called naked fluoride, this quickly proved to be unsuccessful and was abandoned. However, it was seen that solvated fluoride has much better stability and could be used as an ionic liquid anion. This also led to the synthesis of hydroxyl-functionalized triaminocyclopropenium cations.

Synthesis

6.1.1 Anion exchange

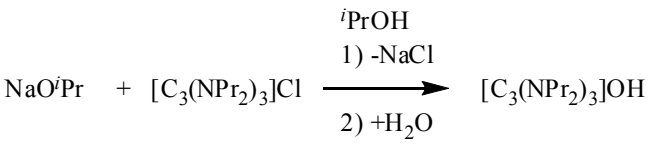
The starting salts for ionic liquid fluorides synthesized in this work were the triaminocyclopropenium chloride salts and commercially-obtained $[C_2MIM]Cl$. The syntheses of the triaminocyclopropenium chloride salts are described in previous chapters.

Three methods were investigated for the exchange of chloride to fluoride anions, with varying degrees of success: anion metathesis with silver fluroide, neutralization of hydroxide with HF acid and anion metathesis with potassium fluoride in ethanol.

Anion metathesis with silver fluoride from the chloride salt is the most direct route, Maiti *et al.*[2] and Vitz *et al.*[9] added silver fluoride to an aqueous solution of a chloride IL which precipitates silver chloride due to its low solubility. This method was used for one synthesis of $[C_3(N(C_2H_4OH)_2)_3]F$ and this resulted in a final chloride content of 1600 ppm, approximately 3% of total anions.

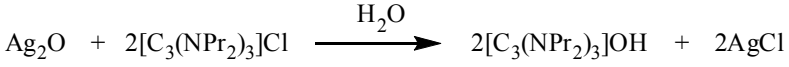
A common and readily accessible source of fluoride is HF acid. HF is a weak acid, so direct metathesis with chloride ionic liquids is not possible, however, the chloride anion can be converted first to a hydroxide anion which is then neutralized with HF. It should also be remembered that triaminocyclopropenium ionic liquids are sensitive to concentrated or heated hydroxide solutions, as discussed previously, with the conversion of triaminocyclopropenium cations to bis(dialkylamino)cyclopropenones. There were two methods trialed for the conversion of chloride to hydroxide anions: via sodium isopropoxide and via silver oxide.

The first method for the exchange of chloride to hydroxide (Scheme) involved mixing isopropanol solutions of sodium isopropoxide and $[C_3(NPr_2)_3]Cl$, which precipitated sodium chloride, leaving the triaminocyclopropenium salt in solution with isopropoxide. When this isopropoxide salt was diluted into water, hydroxide anions were formed, and neutralized with aqueous acid. The chloride content however was 8% of the number of $[C_3(NPr_2)_3]^+$ ions, which would be significant enough to affect any property results.



Scheme 1 – Exchange using sodium isopropoxide

The second method used to exchange chloride to hydroxide was to use silver oxide (Scheme 2). This involved mixing silver oxide with an aqueous solution of the chloride salt, in a blacked-out container. The lower solubility of silver chloride compared to silver oxide means silver chloride will precipitate. Using this method, chloride contents of 500 ppm were obtained. Solutions of $[C_3(NPr_2)_3]F$, $[C_3(CH_2CH_2OH)_3]F$ and $[C_3(NEt_2)_2N(C_2H_4OH)_2]F$ were synthesized using this silver oxide method.



Scheme 2 – Exchange using silver oxide

The final method used for the exchange of chloride to fluoride was the use of potassium fluoride in ethanol.[10] This method is similar to that of the sodium isopropoxide exchange of chloride to hydroxide. It involves partially dissolving potassium fluoride in ethanol, followed by the addition of the chloride salt. The solubility ratio of potassium fluoride to potassium chloride is 25, therefore, due to the lower solubility of potassium chloride, this precipitates out. The ethanol was then removed *in vacuo*, and acetonitrile was added. After cooling, a precipitate of potassium fluoride (and possibly residual chloride) was removed. Ethanol was added and acetonitrile removed *in vacuo* to yield the ethanol solvate. This method was used to synthesize the ethanol solvate of $[C_2MIM]F$, and after

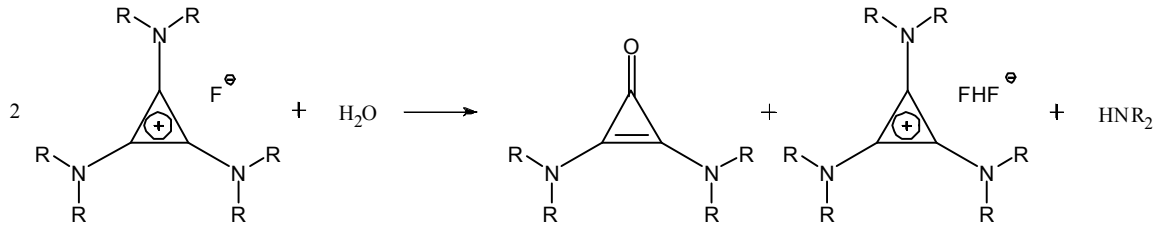
carrying out this exchange three times, the chloride content was 3100 ppm, approximately 2.4% of total anions, and the potassium ion concentration was 220 ppm, approximately 0.15% of $[C_2MIM]^+$. Due to the chloride concentration being higher than preferred, a further step of adding silver fluoride was carried out. The amount of silver fluoride that was added was calculated to lower chloride to less than 100 ppm, without having excess silver present. The final chloride concentration was 70 ppm.

Another method that was considered was the use of an anion exchange column, however, due to the large excess of fluoride salt that is needed for this method it was unsuitable. Maiti *et al.*[2] was able to use a fluoride-loaded anion-exchange column to prepare ionic liquid fluorides, although this was not successful for Vitz *et al.*[9]

6.1.2 From solution to IL

Once a solution of fluoride ionic liquid was obtained the solvent needed to be removed. Due to the reactivity of fluoride, this can be more difficult than for other ionic liquids. As the fluoride anion becomes less solvated, its basicity increases, causing it to react with the cation and likely decomposing it.

The first experiment started with a solution of $[C_3(NPr_2)_3]F$ in water, the water was removed under vacuum on a rotary evaporator at 40 °C. This reduced the water content to approximately 20%, about four water molecules per triaminocyclopropenium fluoride. Further water was not removed under those conditions due to the water forming strong hydrogen bonds to fluoride. When the temperature or vacuum was increased more water was removed, however, due to the heat and the increasing basicity of the fluoride as more water was removed, the ionic liquid totally decomposed to bis(dipropylamino)cyclopropenone and $[C_3(NPr_2)_3]HF_2$ (Scheme 3). Freeze drying was also attempted with the water content dropping to 1.8% and 25% triaminocyclopropenium decomposing to cyclopropenone.



Scheme 3 – Decomposition of $[C_3(NPr_2)_3]F$

Azeotrope drying was then attempted. Other literature had described toluene as a heterogeneous azeotrope to dry ILs,[11] however, this still led to the triaminocyclopropenium fluoride salt being concentrated in a wet phase, and gave 30% cyclopropenone. Therefore, homogeneous azeotropes were investigated whereby water is removed before the ionic liquid is concentrated. Both ethanol and isopropanol will form lower boiling homogeneous azeotropes with water, and both were used successfully. Due to the potential of the ionic salt to break the azeotrope, a large excess of ethanol or isopropanol is used. Isopropanol has the advantage of having a higher percentage of water in the azeotrope, so water can be removed with less additional solvent.

Azeotrope drying was first used to synthesis $[C_3(NPr_2)_3]F.1.9EtOH$, and later $[C_3(NEt_2)_2N(C_2H_4OH)_2]F.1.9EtOH$, $[C_3(N(C_2H_4OH)_2)_3]F$ and $[C_2MIM].1.8EtOH$. During the synthesis of $[C_3(NPr_2)_3]F.1.9EtOH$, repeated additions of dry ethanol produced an ionic liquid fluoride with a water content of 2200 ppm without cyclopropenone forming. The ethanol solvate could not easily be removed, because of the strong hydrogen bonds between the alcohol solvate and fluoride anion provided stability to the ionic liquid fluoride. The fluoride solvates will be discussed in more detail in the next section.

In order to see whether triaminocyclopropenium cations are stable with naked fluoride anions, the ethanol solvate had to be removed. $[C_3(NPr_2)_3]F.1.9EtOH$ had been synthesized by removing ethanol at 40 °C with a low vacuum. However, increasing the temperature or vacuum only resulted in decomposition of the cation. Using another azeotrope, between benzene and ethanol, further ethanol was removed to form a monoethanol solvate: one addition of dried benzene to a sample of the diethanol solvate

leaves 1.36 ethanol molecules per fluoride. After two more additions, this drops to 1.1 ethanol molecule per fluoride. However, significant amounts (17%) of bis(dipropylamino)cyclopropenone were detected in the product. This could be due to deprotonation of ethanol to the alkoxide ion, which then also would nucleophilically attack the triaminocyclopropenium cation, or due to fluoride directly nucleophilically attacking the triaminocyclopropenium cation, and on exposure to the atmosphere, when preparing NMR samples, bis(dipropylamino)cyclopropenone would be formed.

At this point, it was concluded that naked fluoride anions with triaminocyclopropenium cations would not form stable ionic liquid fluorides. However, further progress was made with solvated ionic liquid fluorides.

Fluoride solvates

After it was observed that ethanol solvates of fluoride salts had reasonable stability, this became of interest. The ethanol solvate is similar to the *t*-butanol solvate of tetrabutylammonium fluoride, TBAF(^{t}BuOH)$_4$, which is a fluoride solvate that has been investigated as an anhydrous source of fluoride.[12] However, due to the symmetric shape of the ions and *t*-butanol, and the non-dispersed charges it is a solid.

Larson *et al.*[13] carried out gas phase measurements of the binding energy of fluoride with a variety of Brönsted and Lewis acids. The binding energy of the ethanol to fluoride hydrogen bond was 132 kJ mol^{-1}, a strong hydrogen bond which is not much weaker than that measured for hydrogen fluoride to fluoride (bifluoride) at 161 kJ mol^{-1}. Other measurements have suggested this was low and found a bond energy of 191 kJ mol^{-1}.[14] The strong hydrogen bond suggests that the alcohol solvate can be thought of as a discrete species. Fluorohydrogenate ([F(HF)$_x$]$^-$) ionic liquids are considered as a discrete species, and have received considerable attention in the literature due high conductivities and low viscosities.[15,16]

The solvate molecules do not need to be limited to an alcohol, they just need to be a good hydrogen bond donor. Prompted by earlier work on dimeric and higher order oligomeric

acetic acid anions,[17] Prof. Douglas MacFarlane suggested acetic acid as a solvate molecule. Both the AcOHF and $(AcOH)_2F$ species have been observed previously by NMR at sub ambient temperature.[18]

A comparison between fluoride solvates and deep eutectic solvents can also be made. Deep eutectic solvents are a class of liquids that have many similarities to ionic liquids. They are formed by mixing a solid salt, which has a hydrogen bond acceptor anion, with a hydrogen bond donor compound. For example, a 1:2 mixture of (2-hydroxyethyl)trimethylammonium chloride and urea has a melting point of only 12 °C, much lower than either of the pure compounds, because the urea hydrogen bonds to the chloride, increasing the anion size and decreasing symmetry.

Acetic acid solvate synthesis

A range of acetic acid solvates were synthesized with various amounts of solvate. The aim was for mixtures of 1, 1.5, 2, 2.5 and 3 equivalents of acetic acid per fluoride anion. The acetic acid solvates were synthesized from a starting source material of $[C_2MIM]F.1.8EtOH$. Acetic acid was added to this, and the mixture was dried using ethanol or isopropanol azeotropes under reduced pressure. Due to the strong hydrogen bonds to fluoride and the higher vapour pressure, the alcohol solvent can be easily removed, while only small amounts of acetic acid were lost. Extra acetic acid was added to bring the ratio back to the desired level. ^{1}H-NMR was used to access the precise ratios of acetic acid to $[C_2MIM]^+$, which were 1.01, 1.57, 2.08, 2.44 and 3.22.

The ^{13}C and ^{19}F NMR also provides evidence for the formation of fluoride/acetic acid hydrogen bonded anions. The ^{19}F NMR of $[C_3(NPr_2)_3]F.1.9EtOH$ in D_2O showed a peak at –122.03 ppm and $[C_2MIM]F.1.8EtOH$ at –121.22 ppm, which is the shift for sodium fluoride in D_2O. However, in the various acetic acid mixtures the ^{19}F NMR peak was around –128.8 ppm. This is closer to the shift of F_2H^-, at –142 ppm, suggesting the fluoride environment is more like that of F_2H^-. This could be explained by the strong hydrogen bond between fluoride and acetic acid persisting in the D_2O solution. A similar observation is made by examining the chemical shift of the methyl protons of the acetic

acid. In D_2O, acetic acid is observed at 2.08 ppm and the acetate ion at 1.90 ppm,[19] while for the fluoride acetic acid mixtures the chemical shifts are between 1.94 and 1.98 ppm.

A small signal for F_2H^- was observed and can be explained by the proton being lost from acetic acid and hydrogen bonding to two fluorides. This was undesirable, however, the amount indicated by NMR was not large and no attempt to remove this was made. Removal may not have been possible if it was formed due to an equilibrium process.

Properties

For samples of $[C_2MIM]F.xAcOH$ (x = 1.01, 1.57, 2.08, 2.44, 3.22) and $[C_3(NPr_2)_3]F.1.9EtOH$, the viscosity, conductivity and density were measured. These provide an initial investigation into the physicochemical properties of ethanol and acetic acid fluoride solvates.

Viscosity

The viscosity of the $[C_2MIM]F$ acetic acid mixtures and $[C_3(NPr_2)_3]F.1.9EtOH$ was measured over the temperature range 20 to 50 °C (Table 6-1). The viscosity is similar to or higher than for these cations with DCA or TFSA anions, however, compared to other halide ionic liquids the viscosity is much lower. This is due to the acetic acid or ethanol being a co-solvent with much lower viscosity. While, it is not possible to directly compare the viscosities of the acetic acid and ethanol solvates, due to the different cations and different number of solvate molecules, it is probable that the viscosity of ethanol solvates is lower than the acetic acid solvates if the cation and number of solvate molecules is the same. The viscosity of the ethanol solvate is higher due to the large $[C_3(NPr_2)_3]^+$ cation, however, this difference is not as great as the difference between $[C_2MIM]TFSA$ and $[C_3(NPr_2)_3]TFSA$, with the later salt being approximately five times the viscosity of the first.

Table 6-1 – Viscosity of ethanol and acetic acid fluoride solvates

	η / mPa s						
	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C
$[C_2MIM]F.1.0AcOH$	30.2	24.7	20.2[a]	17.2	14.7	12.7	11.1
$[C_2MIM]F.1.6AcOH$	20.5	17.1	14.8	12.7	11.1	9.71	8.58
$[C_2MIM]F.2.1AcOH$	17.6	14.8	12.7	11.0	9.61	8.45	7.47
$[C_2MIM]F.2.4AcOH$	15.9	13.4	11.5	9.92	8.65	7.60	6.71
$[C_2MIM]F.3.2AcOH$	13.8	11.8	10.1	8.82	7.73	6.81	6.03
$[C_3(NPr_2)_3]F.1.9EtOH$	49.6	40.3	32.7	26.8	22.1	18.1	15.4

Note: [a] Interpolated with VFT equation

As with other ionic liquids, the viscosity falls substantially as temperature increases (Figure 6.1 and Figure 6.2), approximately halving with a 20 °C increase. As was done with other ionic liquids the temperature dependence of viscosity was modeled with the VFT and Arrhenius equations (Table 6-2). D values of between 12.1 and 14.3 were found for the acetic acid solvates and 10.1 for $[C_3(NPr_2)_3]F.1.9EtOH$, suggesting these solvates are slightly less fragile than other ionic liquids with the same cations. The activation energies were between 22 and 31 kJ mol^{-1}, a reflection of the lower viscosity of these solvates compared to ionic liquids in the previous chapter.

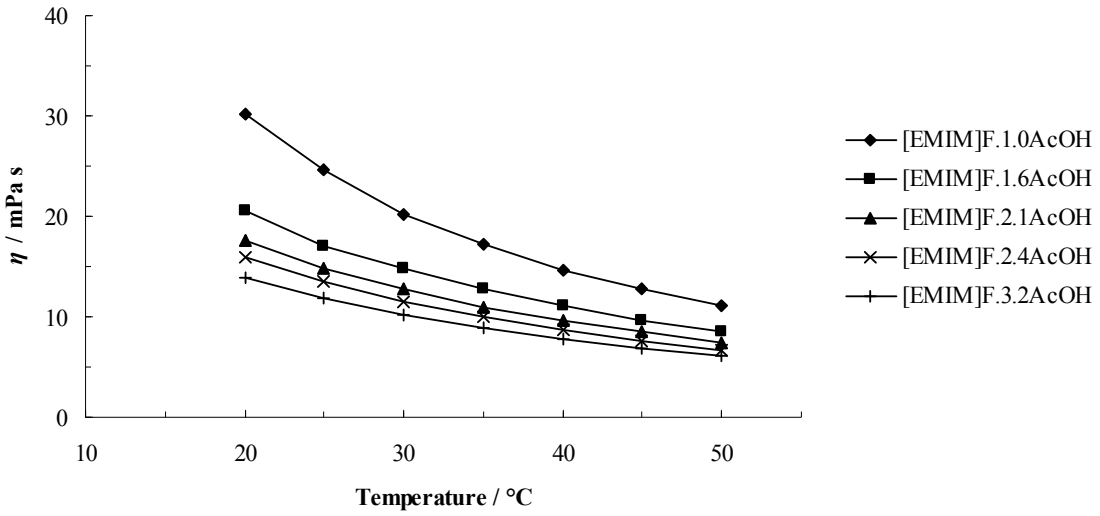


Figure 6.1 – Viscosity versus temperature plot for $[C_2MIM]F.xAcOH$ (x = 1.01, 1.57, 2.08, 2.44, 3.22)

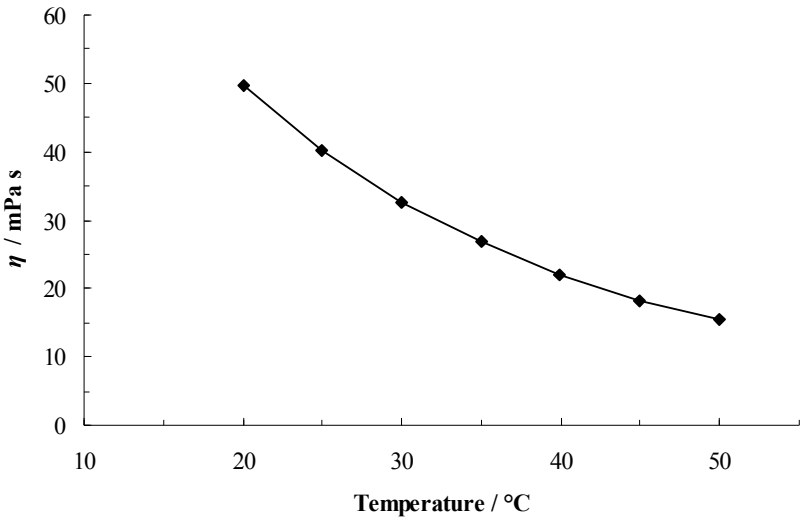


Figure 6.2 – Viscosity versus temperature plot for $[C_3(NPr_2)_3]$F.1.9EtOH

Table 6-2 – Fitting parameters for temperature dependence of viscosity

	η_0 mPa s	B K	T_0 K	D	δ mPa s	A x10^3 mPa s	E_a kJ mol^{-1}	δ mPa s
$[C_2MIM]$F.1.0AcOH	0.029	1290	106	12.1	0.024	0.60	26	0.28
$[C_2MIM]$F.1.6AcOH	0.030	1289	95	13.5	0.030	1.81	23	0.16
$[C_2MIM]$F.2.1AcOH	0.028	1289	93	13.9	0.015	1.76	22	0.12
$[C_2MIM]$F.2.4AcOH	0.024	1289	94	13.8	0.007	1.48	23	0.10
$[C_2MIM]$F.3.2AcOH	0.024	1289	90	14.3	0.004	1.85	22	0.06
$[C_3(NPr_2)_3]$F.1.9EtOH	0.020	1292	128	10.1	0.108	0.15	31	0.12

As the amount of acetic acid (Figure 6.3) is increased the viscosity falls, for example, from 30.2 with 1.0AcOH to 13.8 mPa s with 3.2AcOH at 20 °C. This is due to the acetic acid being a lower viscosity liquid, diluting the more viscous ionic salt, and indicates the presence of an equilibrium between free acetic acid and fluoride-coordinated acetic acid.

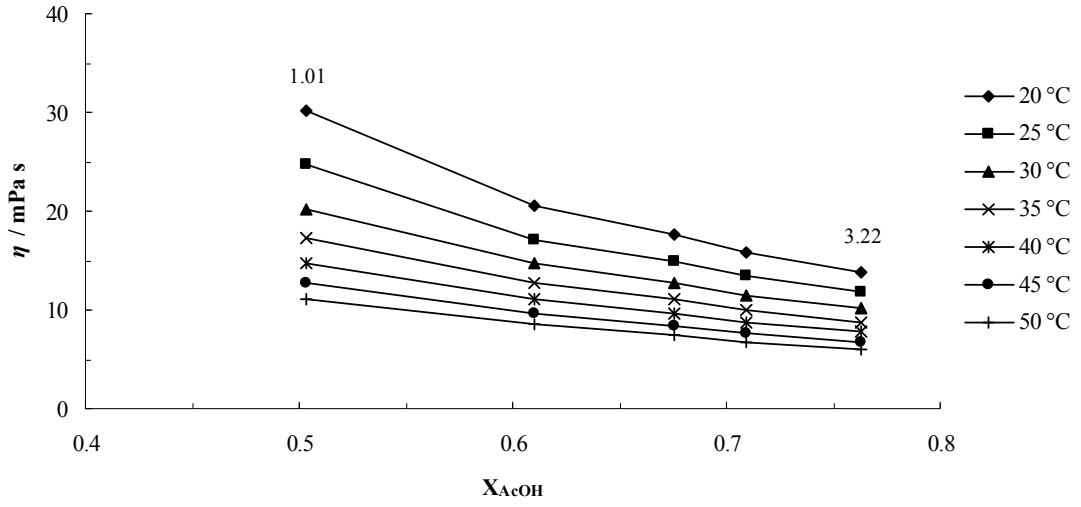


Figure 6.3 – Viscosity versus mole fraction of acetic acid for [C_2MIM]F.xAcOH (x = 1.01, 1.57, 2.08, 2.44, 3.22)

Conductivity

The conductivity of the [C_2MIM]F acetic acid mixtures and [$C_3(NPr_2)_3$]F.1.9EtOH was measured over the temperature range 20 to 40 °C (Table 6-3). The conductivity is similar to or lower than the cations with DCA or TFSA anions, however, compared to other halide ionic liquids the conductivity is much higher. This is a reflection of the trends seen with the viscosity measurements. As with viscosity, it is not possible to directly compare their viscosities of the acetic acid and ethanol solvates, due to the different cations and different number of solvate molecules, it is probable that the conductivity of ethanol solvates is higher than the acetic acid solvates if the cation and number of solvate molecules is the same. The conductivity of the ethanol solvate is lower due to the large $[C_3(NPr_2)_3]^+$ cation, which causes higher viscosity and lowers the number of charge carriers in a given volume.

Table 6-3 – Conductivity of ethanol and acetic acid fluoride solvates

	σ / mS cm^{-1}				
	20 °C	25 °C	30 °C	35 °C	40 °C
$[C_2MIM]F.1.0AcOH$	9.37	10.8	12.4	14.3	16.2
$[C_2MIM]F.1.6AcOH$	11.7	13.2[a]	14.8	17.0	19.1
$[C_2MIM]F.2.1AcOH$	10.8	12.5	14.3	16.2	18.6
$[C_2MIM]F.2.4AcOH$	10.6	11.9	13.4	14.9	16.6
$[C_2MIM]F.3.2AcOH$	10.0	11.5	13.0	14.7	16.4
$[C_3(NPr_2)_3]F.1.9EtOH$	1.89	2.28	2.74	3.24	3.75

Note: [a] Interpolated with Arrhenius equation

As with other ionic liquids, the conductivity increases substantially as the temperature increases (Figure 6.4 and Figure 6.5). As was done with other ionic liquids, the temperature dependence of conductivity was modeled with the Arrhenius equation (Table 6-4). Due to the limited temperature range and limited number of data points, the fitting of the VFT equation did not produce sensible results so are not reported here. The activation energies were between 17 and 26 kJ mol^{-1}.

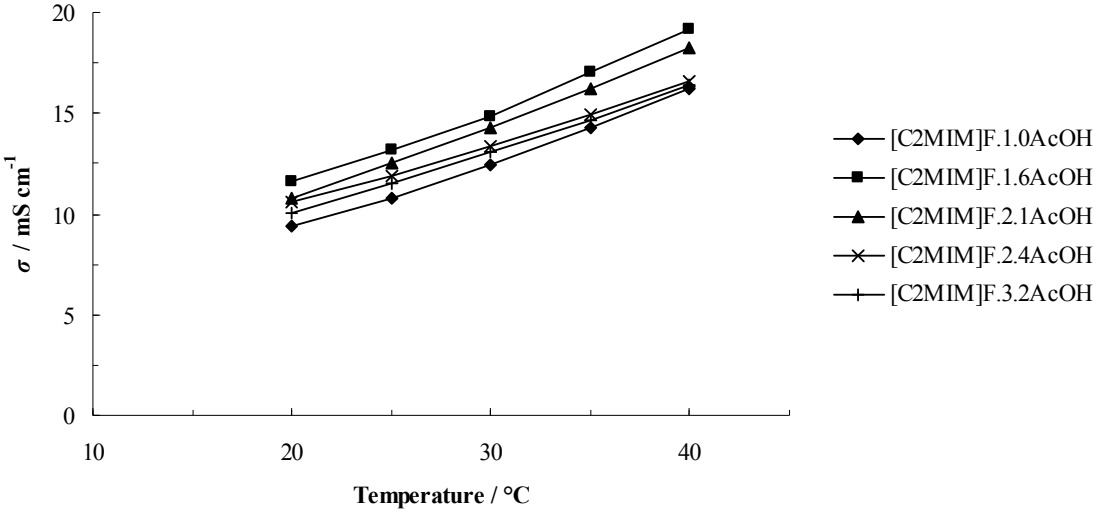


Figure 6.4 – Conductivity versus temperature plot for $[C_2MIM]F.xAcOH$ (x = 1.01, 1.57, 2.08, 2.44, 3.22)

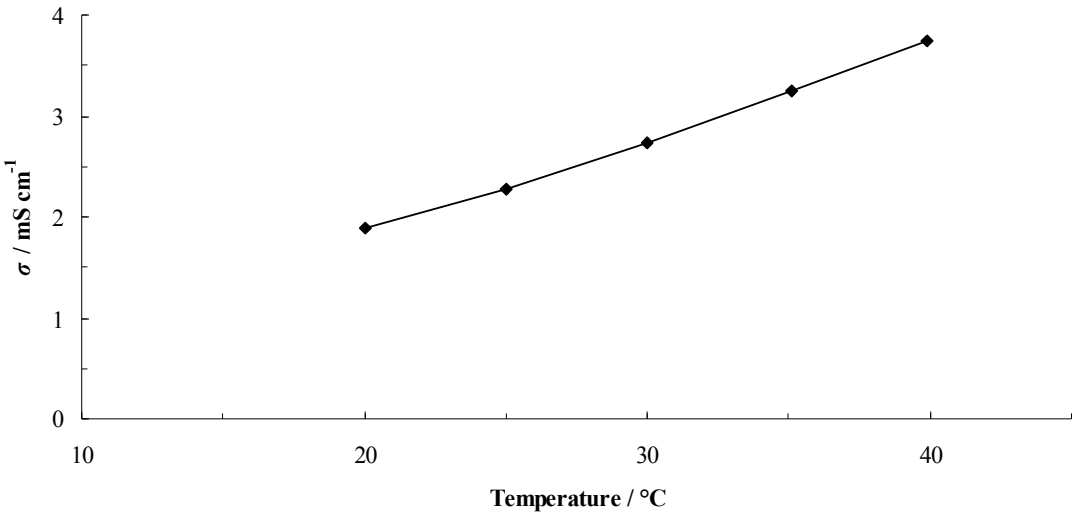


Figure 6.5 – Conductivity versus temperature plot for $[C_3(NPr_2)_3]$F.1.9EtOH

Table 6-4 – Fitting parameters for temperature dependence of conductivity

	A x10^{-4} mS cm^{-1}	E_a kJ mol^{-1}	δ mS cm^{-1}
$[C_2MIM]$F.1.0AcOH	5.16	21	0.03
$[C_2MIM]$F.1.6AcOH	2.81	19	0.12
$[C_2MIM]$F.2.1AcOH	3.86	20	0.07
$[C_2MIM]$F.2.4AcOH	1.24	17	0.01
$[C_2MIM]$F.3.2AcOH	2.25	19	0.05
$[C_3(NPr_2)_3]$F.1.9EtOH	9.19	26	0.03

As the amount of acetic acid (Figure 6.6) increases, the conductivity increases from 9.4 mS cm^{-1} for $[C_2MIM]$F.1.0AcOH to 11.7 mS cm^{-1} for $[C_2MIM]$F.1.6AcOH, and then decreases to 10.0 mS cm^{-1} for $[C_2MIM]$F.3.2AcOH as further acetic acid is added. This is due to the overlap of two competing effects as more acetic acid is added: the molar conductivity increases, due to the viscosity decreasing, but the concentration of ions decreases. The largest relative decrease in viscosity is from 1.0 to 1.6 acetic acid equivalents, and the resulting increase in molar conductivity outweighs the decrease in ion concentration. However, after this point the decrease in ion concentration outweighs the increase in molar conductivity, causing the conductivity to decrease.

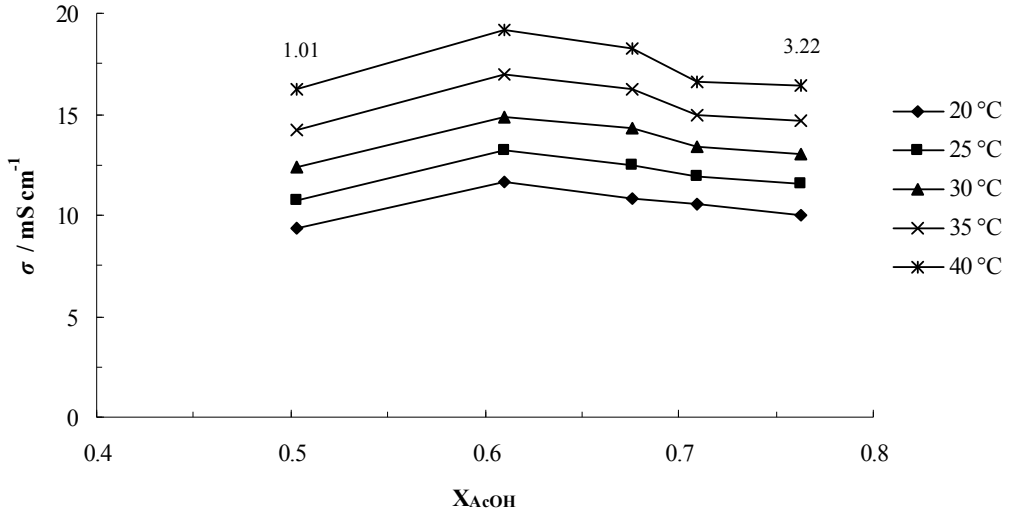


Figure 6.6 – Conductivity versus mole fraction of acetic acid for [C_2MIM]F.xAcOH (x = 1.01, 1.57, 2.08, 2.44, 3.22)

Density

The density for the [C_2MIM]F acetic acid mixtures was measured over the temperature range 20 to 50 °C (Table 6-5 and Figure 6.7). As expected, density decreases as the acetic acid is increased due to the lower density of acetic acid.

Table 6-5 – Density of acetic acid fluoride solvates

	ρ / g mL^{-1}						
	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C
[C_2MIM]F.1.0AcOH	1.125	1.122	1.118	1.115	1.112	1.108	1.105
[C_2MIM]F.1.6AcOH	1.121	1.117	1.114	1.110	1.107	1.103	1.100
[C_2MIM]F.2.1AcOH	1.120	1.116	1.112	1.109	1.105	1.101	1.098
[C_2MIM]F.3.2AcOH	1.118	1.114	1.110	1.106	1.102	1.098	1.094

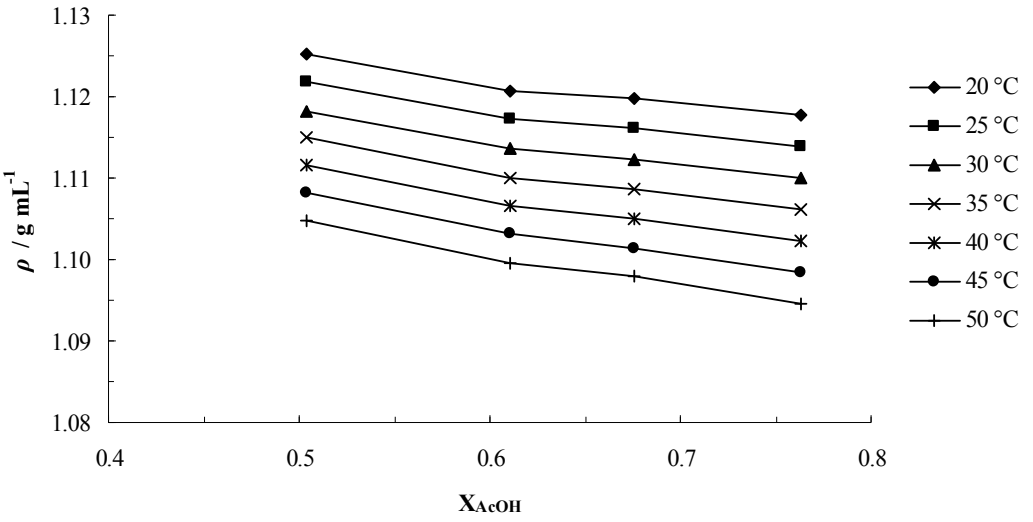


Figure 6.7 – Density versus mole fraction of acetic acid for [C_2MIM]F.xAcOH (x = 1.01, 1.57, 2.08, 2.44, 3.22)

The density was linearly dependent on temperature (Table 6-6).

Table 6-6 – Fitting parameters for temperature dependence of density, $\rho = a - bT$

	$-b$ x10^{-4} g mL^{-1} K^{-1}	a g mL^{-1}	δ x10^{-5}
[C_2MIM]F.1.0AcOH	6.7834	1.3238	2.5
[C_2MIM]F.1.6AcOH	7.0611	1.3276	2.6
[C_2MIM]F.2.1AcOH	7.2967	1.3335	2.6
[C_2MIM]F.3.2AcOH	7.6728	1.3424	2.8

Ionicity

The ionicity of the fluoride solvates was assessed using a Walden plot (Figure 6.8). The Walden product and the deviation from ideal ionic behaviour is shown in Table 6-7. The Walden products for the fluoride solvates are between 0.40 and 0.48 S cm^2 P mol^{-1} and deviations from the ideal ionic behaviour are between 0.32 and 0.40. Since all the fluoride solvate ionic liquids are less than one order of magnitude below the ideal ionic behaviour, they can be classified[20] as good ionic liquids in terms of the ionicity. As a

comparison, $[C_2MIM]F.2.3HF$ has a higher Walden product of 0.76 and a lower ΔW of 0.12.[15]

There was a slight increase in ΔW as the number of acetic acid solvate molecules was increased. This could be due to more opportunity for hydrogen bonding between the proton at the C2 position on the imidazolium ring and oxygen atoms in acetic acid, or could be due to more solvate molecules making aggregates of ions more favourable.

For the Walden plot, density measurements for $[C_2MIM]F.2.4AcOH$ and $[C_3(NPr_2)_3]F.1.9EtOH$ were needed. The density of $[C_2MIM]F.2.4AcOH$ was approximated by averaging the density of $[C_2MIM]F.2.1AcOH$ and $[C_2MIM]F.3.2AcOH$. The density of $[C_3(NPr_2)_3]F.1.9EtOH$ was approximated by that of $[C_3(NPr_2)_3]DCA$, as it is of medium density which minimizes the error . These approximations will increase the error, however, not by a large amount since density does not have a large range for these liquids.

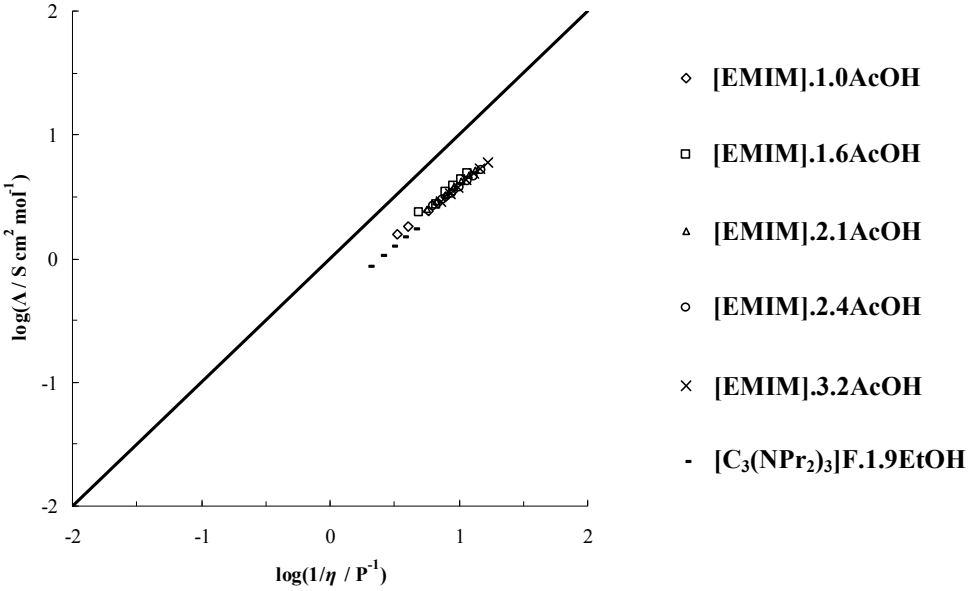


Figure 6.8 – Walden plot of fluoride solvates

Table 6-7 –Walden product and deviation from ideal at 20 °C

	Walden product	ΔW
$[C_2MIM]F.1.0AcOH$	0.48	0.32
$[C_2MIM]F.1.6AcOH$	0.48	0.32
$[C_2MIM]F.2.1AcOH$	0.43	0.36
$[C_2MIM]F.2.4AcOH$	0.42	0.38
$[C_2MIM]F.3.2AcOH$	0.40	0.40
$[C_3(NPr_2)_3]F.1.9EtOH$	0.43	0.37

Thermal Stability

The thermal stability of the fluoride ethanol solvate was investigated using TGA. Thermally stable ionic liquids would be desirable, as they could be used in applications at elevated temperatures, however, the reactivity of fluoride caused concern in this regard. The TGA of the ethanol solvate of $[C_3(NPr_2)_3]F$ (Figure 6.9) shows the weight of the sample starts to decrease at approximately 50 °C. This is likely to be ethanol being lost, which will lead to the decomposition of $[C_3(NPr_2)_3]^+$.

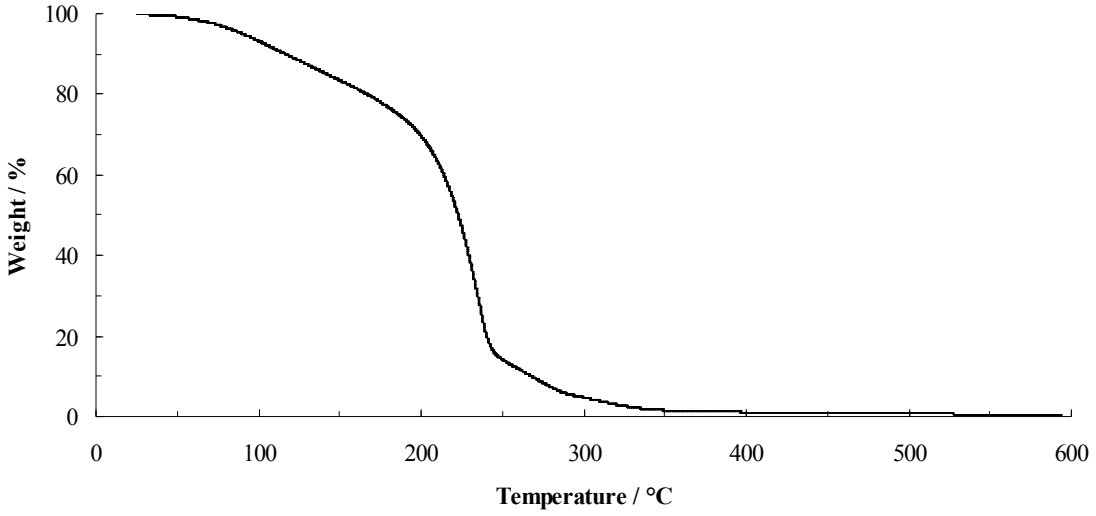


Figure 6.9 – TGA of ethanol solvate of $[C_3(NPr_2)_3]F$ at 10 °C min^{-1}

A sample of (2-hydroxyethyl)trimethylammonium (choline) fluoride hydrate was prepared from the chloride salt using silver oxide and aqueous HF. The TGA is shown below (Figure 6.10). This TGA shows an improved profile compared to the ethanol solvate of $[C_3(NPr_2)_3]F$, with an onset temperature of 139 °C. It should be noted that (2-

hydroxyethyl)trimethylammonium fluoride hydrate is a solid, and no melting point is observed prior to decomposition.

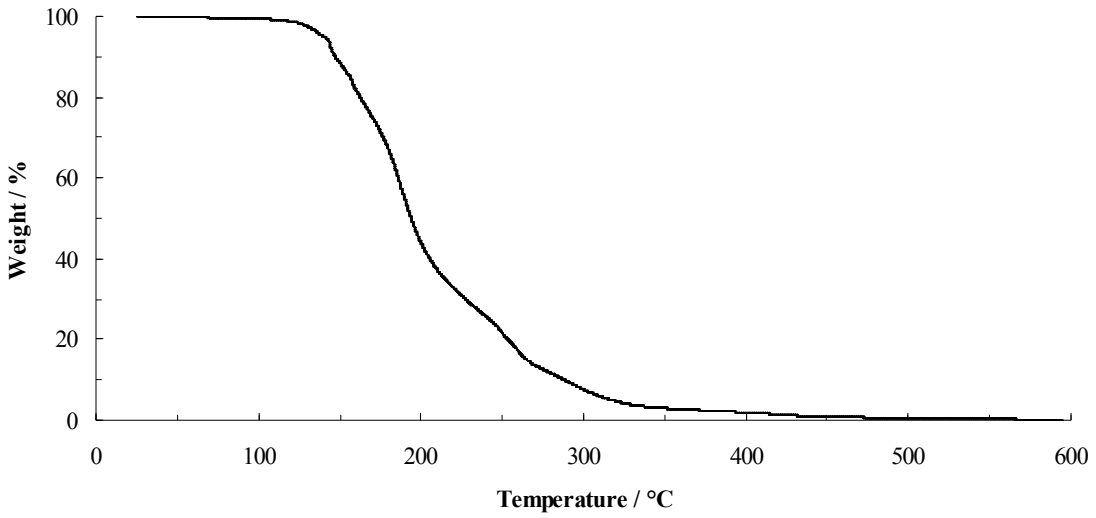


Figure 6.10 – TGA of (2-hydroxyethyl)trimethylammonium fluoride hydrate at 10 °C min^{-1}

The improved thermal stability of (2-hydroxyethyl)trimethylammonium fluoride hydrate suggests that hydroxyl substituents could give thermally-stable fluoride ionic liquids. This led to the syntheses of $[C_3(N(C_2H_4OH)_2)_3]^+$ and $[C_3(NEt_2)_2N(C_2H_4OH)_2]^+$. The synthesis of the cations is described in chapter 4, and the anions were exchanged using the silver oxide or silver fluoride methods.

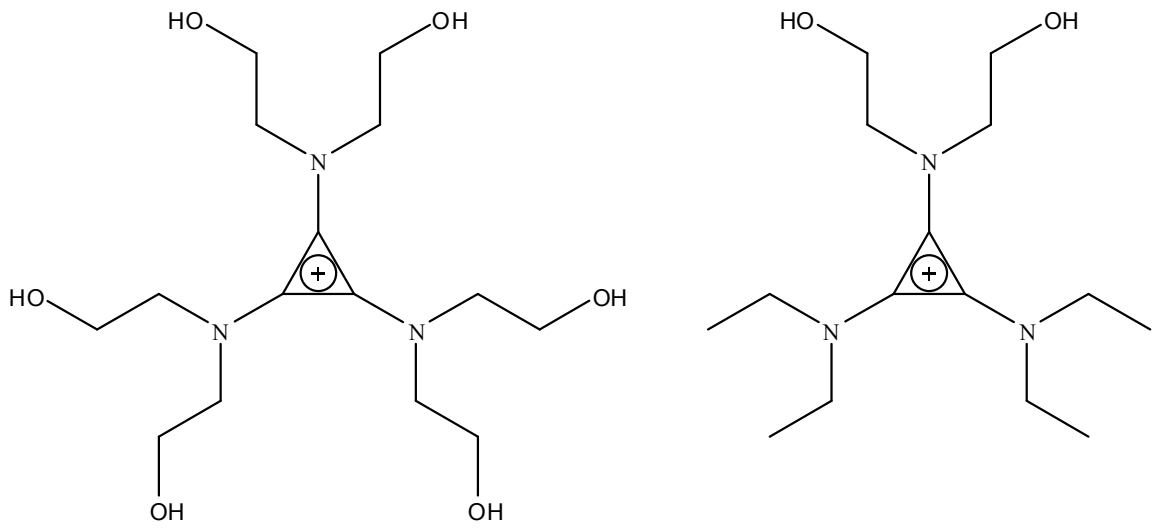


Figure 6.11 - $[C_3(N(C_2H_4OH)_2)_3]^+$ and $[C_3(NEt_2)_2N(C_2H_4OH)_2]^+$

The TGA of $[C_3(N(C_2H_4OH)_2)_3]F$ (Figure 6.12) shows a profile similar to that of (2-hydroxyethyl)trimethylammonium fluoride hydrate, there is little weight loss before the decomposition. Unlike (2-hydroxyethyl)trimethylammonium fluoride hydrate, $[C_3(N(C_2H_4OH)_2)_3]F$ does not decompose upon melting: the melting point was observed at 87 °C, which qualifies this as an ionic liquid. The onset temperature of decomposition at 191 °C is only moderate, and is much lower than other ionic liquids with non-coordinating anions such as TFSA.

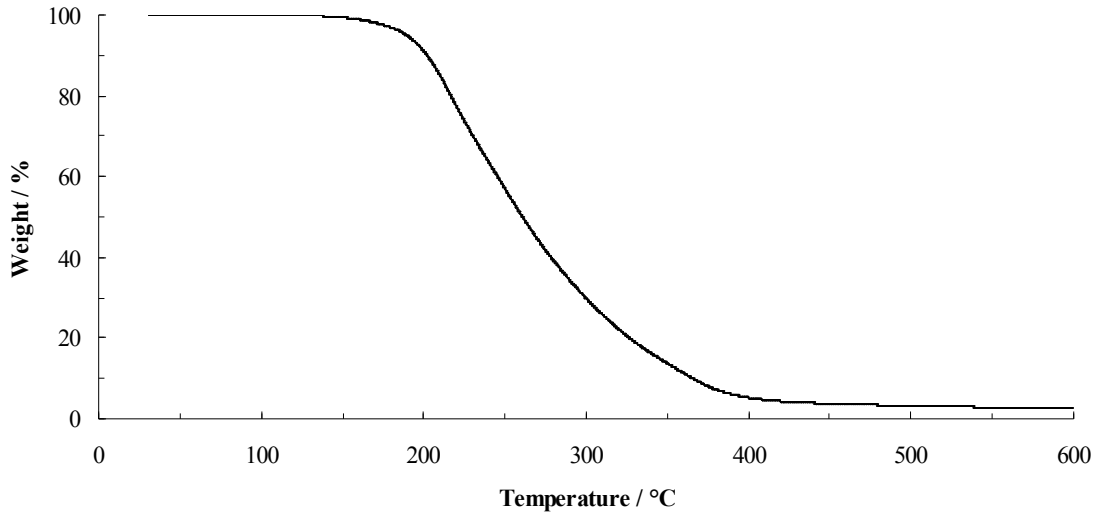


Figure 6.12 – TGA of $[C_3(N(C_2H_4OH)_2)_3]F$ at 10 °C min^{-1}

The TGA of $[C_3(NEt_2)_2N(C_2H_4OH)_2]F$ (Figure 6.13) again shows a profile similar to that of (2-hydroxyethyl)trimethylammonium fluoride hydrate and $[C_3(N(C_2H_4OH)_2)_3]F$, showing that hydroxyl functional groups do stabilize the fluoride anion. $[C_3(NEt_2)_2N(C_2H_4OH)_2]F$ was a viscous yellow liquid at ambient temperature, although it is thought that this could be a supercooled state, due to the high viscosity. The onset temperature was 175 °C, lower than $[C_3(N(C_2H_4OH)_2)_3]F$. It should be noted that more care had to be taken when drying $[C_3(NEt_2)_2N(C_2H_4OH)_2]F$, whereas $[C_3(N(C_2H_4OH)_2)_3]F$ was less sensitive to residual water due to more hydroxyl groups per fluoride which means hydroxide anions will not be formed.

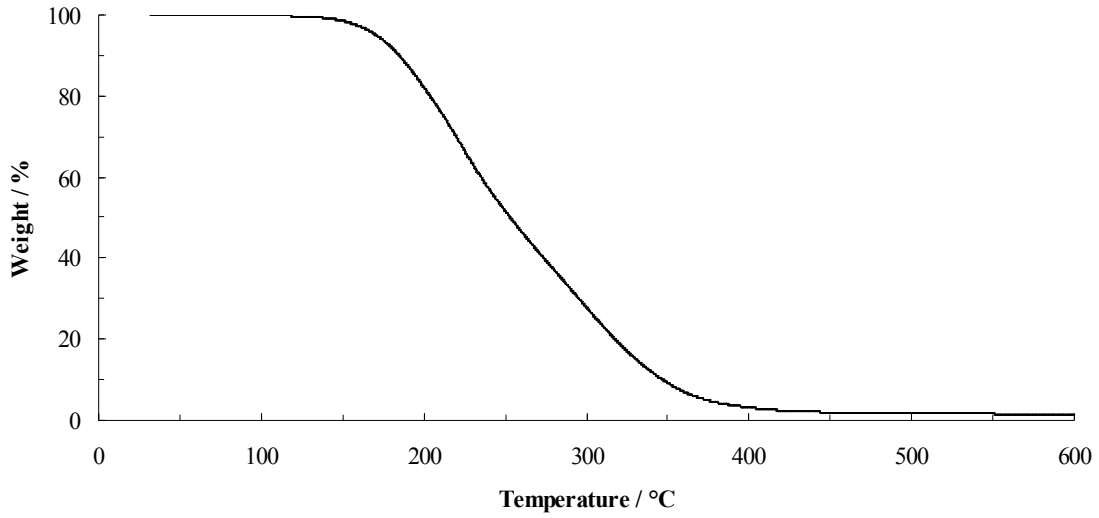


Figure 6.13 – TGA of $[C_3(NEt_2)_2N(C_2H_4OH)_2]F$ at 10 °C min^{-1}

DSC

The thermal behaviour of $[C_2MIM]F.1.6AcOH$ and $[C_2MIM]F.3.2AcOH$ was examined using DSC. Glass transitions were observed at –92 for $[C_2MIM]F.1.6AcOH$ and –95 °C for $[C_2MIM]F.3.2AcOH$. No melting points were observed.

Conclusions

This preliminary investigation into ionic liquid fluorides exchanged chloride anions to fluoride anions using one of three methods: anion metathesis with silver fluroide, anion metathesis using aqueous silver oxide followed by neutralization with HF acid or anion metathesis with potassium fluoride in ethanol. The fluoride salts were then isolated using homogeneous azetrope drying.

Whereas naked fluoride salts were not stable, fluoride solvates with ethanol and acetic acid were stable due strong hydrogen bonds. $[C_3(NPr_2)_3]F.1.9EtOH$ and $[C_2MIM]F.xAcOH$ (x = 1.0, 1.6, 2.1, 2.4, 3.2) were synthesized and their viscosity, conductivity and density were measured. The increasing amount of acetic acid solvate decreased the viscosity and density, while the conductivity peaked for $[C_2MIM]F.1.6AcOH$.

The thermal stability of $[C_3(NPr_2)_3]F.1.9EtOH$ was not good, which led to the synthesis of $[C_3(N(C_2H_4OH)_2)_3]F$ and $[C_3(NEt_2)_2N(C_2H_4OH)_2]F$, which had much better thermal stability and were stable as unsolvated ionic liquids fluorides, although not a naked fluoride as strong hydrogen bonds will be present.

References

(1) Mallik, B. S.; Siepmann, J. I. *J. Phys. Chem. B* **2010**, *114*, 12577-12584.

(2) Maiti, A.; Pagoria, P. F.; Gash, A. E.; Han, T. Y.; Orme, C. A.; Gee, R. H.; Fried, L. E. *Phys. Chem. Chem. Phys.* **2008**, *10*, 5050-5056.

(3) Christe, K. O.; Jenkins, H. D. B. *J. Am. Chem. Soc.* **2003**, *125*, 9457-9461.

(4) Sun, H.; DiMagno, S. G. *J. Am. Chem. Soc.* **2005**, *127*, 2050-2051.

(5) Trewin, A.; Darling, G. R.; Cooper, A. I. *New J. Chem.* **2008**, *32*, 17-20.

(6) Quinn, R.; Appleby, J. B.; Pez, G. P. *J. Am. Chem. Soc.* **1995**, *117*, 329-335.

(7) Turner, E. A.; Pye, C. C.; Singer, R. D. *J. Phys. Chem. A* **2003**, 2277-2288.

(8) Swatloski, R. P.; Holbrey, J. D.; Rogers, R. D. *Green Chem.* **2003**, 361-363.

(9) Vitz, J.; Erdmenger, T.; Haenscha, C.; Schubert, U. S. *Green Chem., 2009, 11, 417–424* **2009**, *11*, 417-424.

(10) Dermeik, S.; Sasson, Y. *J. Org. Chem.* **1989**, *54*, 4827-4829.

(11) Zhao, C.; Burrell, G.; Torriero, A. A. J.; Separovic, F.; Dunlop, N. F.; MacFarlane, D. R.; Bond, A. M. *J. Phys. Chem. B* **2008**, *112*, 6923-6936.

(12) Kim, D. W.; Jeong, H.-J.; Lim, S. T.; Sohn, M.-H. *Angew. Chem. Int. Ed.* **2008**, *47*, 8404-8406.

(13) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1983**, *105*, 2944-2950.

(14) Wenthold, P. G.; Squires, R. R. *J. Phys. Chem.* **1995**, *99*, 2002-2005.

(15) Hagiwara, R.; Matsumoto, K.; Nakamori, Y.; Tsuda, T.; Ito, Y.; Matsumoto, H.; Momota, K. *J. Electrochem. Soc* **2003**, *150*, D195-D199.

(16) Hagiwara, R.; Hirashige, T.; Tsuda, T.; Ito, Y. *J. Fluorine Chem.* **1999**, 1-3.

(17) Johansson, K. M.; Izgorodin, E. I.; Forsyth, M.; MacFarlane, D. R.; Seddon, K. R. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2972-2978.

(18) Golubev, N. S.; Tolstoy, P. M.; Smirnov, S. N.; Denisov, G. S.; Limbach, H.-H. *J. Mol. Struct.* **2004**, *700*, 3-12.

(19) Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512-7515.

(20) Xu, W.; Cooper, E. I.; Angell, C. A. *J. Phys. Chem. B* **2003**, *107*, 6170-6178.

Appendix

Appendix: Crystallography

Tables A-1 to A-15 list the crystal data, X-ray experimental details and bond lengths of the alkyl substituents for the crystal structures discussed in this thesis. Using Olex2,[1] the structure was solved with the XS[2] structure solution program using Direct Methods and refined with the XL[3] refinement package using Least Squares minimisation.

References

(1) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.

(2) XS, G.M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122

(3) XL, G.M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122

Table A-1 – Crystal data and structure refinement for $[C_3(NMe_2)_3]$TFSA.

Empirical formula	$C_{11}H_{18}N_4O_4F_6S_2$	
Formula weight	448.41	
Temperature (K)	113.15	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 20.8556(5) Å	α = 90°
	b = 14.7302(4) Å	β = 101.824(2)°
	c = 18.6770(5) Å	γ = 90°
Volume ($Å^3$)	6616.0(3)	
Z	12	
Density (calculated) (mg mm^{-3})	1.541	
Absorption coefficient (mm^{-1})	0.363	
F(000)	2676	
Crystal size (mm^3)	0.74 × 0.51 × 0.08	
2 Theta range for data collection	3.4 to 50.1°	
Index ranges	$-24 \leq h \leq 24$	
	$-17 \leq k \leq 17$	
	$-22 \leq l \leq 22$	
Reflections collected	100470	
Independent reflections	9956 [R(int) = 0.0582]	
Data / restraints / parameters	9956 / 0 / 748	
Goodness-of-fit on F^2	1.007	
Final R indexes [I≥2σ(I)]	R_1 = 0.0374, wR_2 = 0.0855	
Final R indexes (all data)	R_1 = 0.0620, wR_2 = 0.0999	
Largest diff. peak and hole (e $Å^{-3}$)	0.31, –0.35	

Table A-2 – Crystal data and structure refinement for $[C_3(NPr_2)_3]$TFSA.

Empirical formula	$C_{23}H_{42}N_4O_4F_6S_2$	
Formula weight	616.73	
Temperature (K)	296(2)	
Crystal system	Monoclinic	
Space group	C_2	
Unit cell dimensions	a = 34.4583(11) Å	α = 90°
	b = 10.0845(4) Å	β = 106.77(2)°
	c = 19.2426(7) Å	γ = 90°
Volume (Å^3)	6402.3(4)	
Z	8	
Density (calculated) (mg mm^{-3})	1.155	
Absorption coefficient (mm^{-1})	0.109	
F(000)	2368	
Crystal size (mm^3)	0.47 × 0.36 × 0.29	
2 Theta range for data collection	2.2 to 52.0°	
Index ranges	$-42 \leq h \leq 42$	
	$-12 \leq k \leq 12$	
	$-23 \leq l \leq 23$	
Reflections collected	66503	
Independent reflections	12617 [R(int) = 0.0545]	
Data / restraints / parameters	12617 / 1 / 716	
Goodness-of-fit on F^2	1.084	
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0381, wR_2 = 0.0986	
Final R indexes (all data)	R_1 = 0.0527, wR_2 = 0.1196	
Largest diff. peak and hole (e Å^{-3})	0.42, –0.48	

Table 0-3 – Crystal data and structure refinement for $[C_3(NPr_2)_3]DCA$.

Empirical formula	$C_{23}H_{42}N_6$	
Formula weight	402.63	
Temperature (K)	296(2)	
Crystal system	Monoclinic	
Space group	C_2/c	
Unit cell dimensions	a = 21.8840(7) Å	α = 90°
	b = 9.4228(3) Å	β = 113.472(2)°
	c = 27.0076(11) Å	γ = 90°
Volume ($Å^3$)	5108.4(3)	
Z	10	
Density (calculated) (mg mm^{-3})	1.184	
Absorption coefficient (mm^{-1})	0.075	
F(000)	1840	
Crystal size (mm^3)	0.51 × 0.50 × 0.38	
2 Theta range for data collection	3.3 to 55.0°	
Index ranges	$-28 \leq h \leq 28$	
	$-12 \leq k \leq 12$	
	$-35 \leq l \leq 35$	
Reflections collected	55815	
Independent reflections	5876 [R(int) = 0.0447]	
Data / restraints / parameters	5876 / 0 / 297	
Goodness-of-fit on F^2	1.160	
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0444$, $wR_2 = 0.1369$	
Final R indexes (all data)	$R_1 = 0.0744$, $wR_2 = 0.1665$	
Largest diff. peak and hole (e $Å^{-3}$)	0.34, –0.48	

Table A-4 – Bond lengths of alkyl substituents of $[C_3(NMe_2)_3]TFSA$.

		Å			Å
N10	C11	1.454(3)	N50	C52	1.447(4)
N10	C12	1.456(3)	N60	C61	1.449(3)
N20	C21	1.446(4)	N60	C62	1.448(3)
N20	C22	1.448(4)	N70	C71	1.453(4)
N30	C31	1.453(3)	N70	C72	1.449(4)
N30	C32	1.457(3)	N80	C81	1.458(3)
N40	C41	1.451(4)	N80	C82	1.455(3)
N40	C42	1.447(4)	N90	C91	1.454(3)
N50	C51	1.455(4)	N90	C92	1.453(3)

Table A-5 – Bond lengths of alkyl substituents of $[C_3(NPr_2)_3]$TFSA.

		Å			Å
N1	C11A	1.461(4)	N1-	C11A-	1.468(4)
N1	C12A	1.461(3)	N1-	C12A-	1.464(4)
N2	C21A	1.462(3)	N2-	C21A-	1.454(4)
N2	C22A	1.457(4)	N2-	C22A-	1.463(3)
N3	C31A	1.458(4)	N3-	C31A-	1.469(3)
N3	C32A	1.464(3)	N3-	C32A-	1.480(4)
C11A	C11B	1.515(4)	C11A-	C11B-	1.501(5)
C11B	C11C	1.515(4)	C11B-	C11C-	1.540(5)
C12A	C12B	1.518(4)	C12A-	C12B-	1.501(4)
C12B	C12C	1.522(4)	C12B-	C12C-	1.513(5)
C21A	C21B	1.507(4)	C21A-	C21B-	1.516(4)
C21B	C21C	1.509(4)	C21B-	C21C-	1.521(5)
C22A	C22B	1.502(4)	C22A-	C22B-	1.513(4)
C22B	C22C	1.515(5)	C22B-	C22C-	1.514(5)
C31A	C31B	1.521(4)	C31A-	C31B-	1.503(4)
C31B	C31C	1.514(5)	C31B-	C31C-	1.527(4)
C32A	C32B	1.510(4)	C32A-	C32B-	1.501(4)
C32B	C32C	1.523(5)	C32B-	C32C-	1.527(5)

Table A-6 – Bond lengths of alkyl substituents of $[C_3(NPr_2)_3]$DCA.

		Å			Å
N1	C12A	1.4649(17)	C21A	C21B	1.514(2)
N1	C11A	1.4703(17)	C21B	C21C	1.517(3)
N2	C22A	1.4635(18)	C22A	C22B	1.511(2)
N2	C21A	1.4669(18)	C22B	C22C	1.528(2)
N3	C31A	1.4760(18)	C31A	C31B	1.520(2)
N3	C32A-	1.496(3)	C31B	C31C	1.519(2)
N3	C32A	1.538(6)	C32A	C32B	1.508(9)
C11A	C11B	1.5188(18)	C32A-	C32B-	1.515(3)
C11B	C11C	1.5187(19)	C32B	C32C	1.551(13)
C12A	C12B	1.5194(18)	C32B-	C32C-	1.508(5)
C12B	C12C	1.512(2)			

Table A-7 – Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for [$C_3(NMe_2)_3$]TFSA. U(eq) is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

	x	*y*	*z*	U(eq)		*x*	*y*	*z*	U(eq)
C1	0.27922(12)	0.59521(17)	0.46505(13)	0.0271(6)	F33	–0.29742(8)	0.46858(12)	0.31772(10)	0.0531(5)
C10	–0.15156(14)	0.8858(2)	0.43796(15)	0.0402(7)	F41	–0.52200(10)	0.35167(15)	0.43508(10)	0.0699(6)
C11	0.32274(16)	0.44761(19)	0.45016(16)	0.0451(7)	F42	–0.53950(9)	0.27663(14)	0.33472(10)	0.0653(6)
C12	0.37530(14)	0.5865(2)	0.41216(15)	0.0417(7)	F43	–0.45224(10)	0.25425(13)	0.41524(11)	0.0653(5)
C2	0.22873(12)	0.60066(17)	0.50228(13)	0.0281(6)	F51	–0.05795(9)	0.62733(15)	0.39043(12)	0.0728(6)
C20	–0.33392(14)	0.82828(19)	0.57030(16)	0.0382(7)	F52	0.01754(10)	0.53311(14)	0.43797(9)	0.0650(6)
C21	0.17956(18)	0.4613(2)	0.53014(19)	0.0574(9)	F53	–0.02463(9)	0.52628(12)	0.32411(9)	0.0535(5)
C22	0.14598(14)	0.6095(2)	0.57559(15)	0.0448(7)	F61	0.23309(8)	0.66911(14)	0.30070(10)	0.0607(5)
C3	0.25521(12)	0.67885(17)	0.48026(12)	0.0270(6)	F62	0.19665(9)	0.62277(13)	0.19096(9)	0.0569(5)
C30	–0.30743(13)	0.4066(2)	0.26517(16)	0.0389(7)	F63	0.14505(8)	0.72586(11)	0.23653(9)	0.0477(4)
C31	0.30939(15)	0.8130(2)	0.44964(18)	0.0470(8)	N10	0.31980(10)	0.54468(14)	0.43565(11)	0.0319(5)
C32	0.21661(14)	0.82380(19)	0.51419(15)	0.0394(7)	N2	–0.27415(10)	0.85739(14)	0.45788(11)	0.0292(5)
C4	–0.44794(12)	0.89691(17)	0.35985(14)	0.0317(6)	N20	0.18647(11)	0.55889(15)	0.53529(12)	0.0362(5)
C40	–0.49353(14)	0.3172(2)	0.38388(16)	0.0416(7)	N30	0.25569(11)	0.76861(14)	0.47448(11)	0.0311(5)
C41	–0.4945(2)	1.0420(2)	0.37525(19)	0.0671(11)	N4	–0.42817(10)	0.35877(14)	0.27905(11)	0.0281(5)
C42	–0.53764(15)	0.8984(2)	0.42212(16)	0.0513(8)	N40	–0.49042(11)	0.94484(16)	0.38825(14)	0.0427(6)
C5	–0.39621(12)	0.89389(18)	0.32477(15)	0.0335(6)	N5	0.11660(10)	0.60325(14)	0.35774(11)	0.0291(5)
C50	–0.00538(14)	0.5825(2)	0.37924(15)	0.0410(7)	N50	–0.35317(11)	0.93615(17)	0.29378(14)	0.0455(6)
C51	–0.35018(18)	1.0348(2)	0.2965(2)	0.0688(11)	N60	–0.42459(11)	0.72466(15)	0.34776(13)	0.0365(5)
C52	–0.31100(15)	0.8842(3)	0.25652(17)	0.0591(10)	N70	–0.02122(11)	0.70468(15)	0.11306(12)	0.0339(5)
C6	–0.42294(12)	0.81423(17)	0.34469(14)	0.0287(6)	N80	–0.14638(11)	0.67654(14)	0.22267(11)	0.0323(5)
C60	0.17965(13)	0.6501(2)	0.25250(15)	0.0363(6)	N90	–0.07882(10)	0.47589(14)	0.14815(11)	0.0296(5)
C61	–0.37749(14)	0.6694(2)	0.32024(16)	0.0429(7)	O11	–0.21902(9)	0.74139(13)	0.40074(10)	0.0409(5)
C62	–0.47761(14)	0.67970(19)	0.37297(17)	0.0438(7)	O12	–0.17783(9)	0.76875(13)	0.53207(9)	0.0368(4)
C7	–0.05884(12)	0.65055(16)	0.14355(12)	0.0249(5)	O21	–0.34389(9)	0.97410(13)	0.49392(11)	0.0425(5)
C71	0.02698(14)	0.6687(2)	0.07441(15)	0.0452(7)	O22	–0.23896(8)	0.94412(12)	0.57813(9)	0.0333(4)

	x	*y*	*z*	U(eq)		*x*	*y*	*z*	U(eq)
C72	–0.02318(17)	0.8021(2)	0.12293(18)	0.0517(8)	O31	–0.36253(9)	0.25385(13)	0.22396(10)	0.0427(5)
C8	–0.10638(12)	0.64020(16)	0.18387(12)	0.0248(5)	O32	–0.32725(10)	0.28186(14)	0.35582(10)	0.0456(5)
C81	–0.14950(15)	0.77491(19)	0.22987(17)	0.0464(8)	O41	–0.40344(9)	0.43987(13)	0.40241(9)	0.0367(4)
C82	–0.19137(14)	0.6201(2)	0.25326(15)	0.0404(7)	O42	–0.50535(9)	0.46618(13)	0.31281(11)	0.0412(5)
C9	–0.08026(11)	0.56493(16)	0.15668(12)	0.0238(5)	O51	0.07045(10)	0.71528(13)	0.42768(9)	0.0397(5)
C91	–0.02936(14)	0.43317(19)	0.11473(16)	0.0393(7)	O52	0.02437(8)	0.70912(12)	0.29588(9)	0.0315(4)
C92	–0.12135(13)	0.41717(17)	0.18020(15)	0.0345(6)	O61	0.07652(9)	0.54712(13)	0.22680(10)	0.0411(5)
F11	–0.09669(9)	0.84305(15)	0.43177(11)	0.0682(6)	O62	0.17770(10)	0.48933(13)	0.30501(12)	0.0503(5)
F12	–0.17540(10)	0.92507(13)	0.37491(9)	0.0606(5)	S1	–0.20884(3)	0.80215(4)	0.46185(3)	0.02856(15)
F13	–0.13601(9)	0.94922(12)	0.48845(9)	0.0550(5)	S2	–0.29254(3)	0.91239(4)	0.52332(3)	0.02795(15)
F21	–0.38534(9)	0.79290(14)	0.52592(10)	0.0655(6)	S3	–0.35879(3)	0.31291(4)	0.28531(3)	0.03053(16)
F22	–0.35465(9)	0.86800(13)	0.62546(10)	0.0573(5)	S4	–0.45250(3)	0.40727(4)	0.34353(3)	0.02742(15)
F23	–0.29418(9)	0.76150(11)	0.59849(10)	0.0528(5)	S5	0.05551(3)	0.66427(4)	0.36139(3)	0.02657(15)
F31	–0.24899(8)	0.37465(13)	0.25911(12)	0.0650(6)	S6	0.13166(3)	0.56089(4)	0.28539(4)	0.03098(16)
F32	–0.33298(9)	0.44737(13)	0.20310(10)	0.0633(5)					

Table A-8 – Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for [$C_3(NPr_2)_3$]TFSA. U(eq) is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

	x	*y*	*z*	U(eq)		*x*	*y*	*z*	U(eq)
C1	0.38255(7)	0.1160(3)	0.29890(14)	0.0254(6)	C32B-	0.09689(10)	0.9199(3)	0.2433(2)	0.0473(8)
C1-	0.11817(7)	0.5524(3)	0.13171(14)	0.0262(6)	C32C	0.31710(13)	0.4060(5)	0.08254(19)	0.0675(12)
C11A	0.37282(9)	0.0480(3)	0.17515(15)	0.0355(7)	C32C-	0.07565(11)	1.0401(4)	0.2007(3)	0.0650(11)
C11A-	0.06899(9)	0.6674(3)	0.03370(16)	0.0365(7)	C4	0.46765(9)	–0.0779(3)	0.76902(17)	0.0389(7)
C11B	0.34787(9)	–0.0662(3)	0.13424(16)	0.0391(7)	C4-	0.22923(8)	0.7376(3)	0.11204(16)	0.0368(7)
C11B-	0.08655(11)	0.7607(3)	–0.01006(19)	0.0488(8)	C5	0.52047(8)	0.3676(3)	0.71736(17)	0.0393(7)
C11C	0.32167(10)	–0.0218(4)	0.06036(17)	0.0493(9)	C5-	0.28456(9)	0.9365(3)	0.36320(17)	0.0383(7)
C11C-	0.05557(15)	0.8706(4)	–0.0422(2)	0.0781(14)	F1	0.49186(6)	–0.1685(2)	0.75504(12)	0.0557(5)
C12A	0.41577(7)	–0.0852(3)	0.28007(15)	0.0278(6)	F1-	0.24009(6)	0.8528(2)	0.09115(9)	0.0486(5)
C12A-	0.09283(8)	0.4388(3)	0.01624(15)	0.0297(6)	F2	0.43905(5)	–0.0518(2)	0.70761(10)	0.0563(5)

	x	*y*	*z*	U(eq)		*x*	*y*	*z*	U(eq)
C12B	0.39673(8)	–0.1940(3)	0.31391(18)	0.0370(7)	F2-	0.18937(5)	0.7350(2)	0.09612(10)	0.0570(6)
C12B-	0.05921(9)	0.3451(3)	0.01772(19)	0.0442(8)	F3	0.44945(7)	–0.1297(2)	0.81479(12)	0.0662(6)
C12C	0.42592(11)	–0.3099(4)	0.3371(2)	0.0609(11)	F3-	0.24060(6)	0.6442(2)	0.07397(11)	0.0621(6)
C12C-	0.05567(12)	0.2335(4)	–0.0362(2)	0.0712(12)	F4	0.56058(5)	0.3631(2)	0.73602(12)	0.0601(6)
C2	0.38951(7)	0.1641(3)	0.36840(14)	0.0230(5)	F4-	0.31184(5)	0.8416(2)	0.36984(11)	0.0582(6)
C2-	0.14296(7)	0.4829(3)	0.18944(14)	0.0238(6)	F5	0.50935(6)	0.4074(2)	0.77333(12)	0.0582(5)
C21A	0.43600(8)	0.0519(3)	0.47138(15)	0.0275(6)	F5-	0.26059(6)	0.9016(2)	0.40225(10)	0.0581(6)
C21A-	0.16180(8)	0.2616(3)	0.16589(16)	0.0322(6)	F6	0.50873(6)	0.4586(2)	0.66532(13)	0.0653(6)
C21B	0.42211(9)	–0.0422(3)	0.52016(16)	0.0377(7)	F6-	0.30390(7)	1.0458(2)	0.39140(12)	0.0703(7)
C21B-	0.19554(9)	0.2764(3)	0.13042(17)	0.0415(7)	N1	0.38855(7)	0.0265(2)	0.25333(12)	0.0289(5)
C21C	0.45504(11)	–0.1407(3)	0.55457(18)	0.0515(9)	N1-	0.09581(6)	0.5550(2)	0.06302(12)	0.0305(5)
C21C-	0.19480(13)	0.1650(4)	0.0768(2)	0.0662(11)	N2	0.40640(6)	0.1552(2)	0.43982(11)	0.0256(5)
C22A	0.40448(8)	0.2689(3)	0.48545(15)	0.0288(6)	N2-	0.16052(6)	0.3689(2)	0.21560(12)	0.0275(5)
C22A-	0.18520(8)	0.3556(3)	0.29112(14)	0.0315(6)	N3	0.34117(6)	0.3375(2)	0.28569(12)	0.0291(5)
C22B	0.43503(9)	0.3748(3)	0.48489(18)	0.0395(7)	N3-	0.13972(6)	0.7239(2)	0.23748(12)	0.0318(5)
C22B-	0.16394(10)	0.2783(4)	0.33683(18)	0.0495(9)	N4	0.51645(6)	0.1136(2)	0.74926(13)	0.0320(5)
C22C	0.42953(12)	0.4955(4)	0.5279(2)	0.0620(11)	N4-	0.23524(6)	0.8281(2)	0.24412(12)	0.0290(5)
C22C-	0.19113(15)	0.2624(5)	0.4137(2)	0.0809(14)	O1	0.52473(7)	0.0249(3)	0.86992(12)	0.0594(7)
C3	0.36452(7)	0.2331(3)	0.31108(14)	0.0253(6)	O1-	0.29541(5)	0.7130(2)	0.21754(10)	0.0323(4)
C3-	0.13461(7)	0.6152(3)	0.19731(14)	0.0257(6)	O2	0.46446(7)	0.1588(3)	0.81728(12)	0.0517(6)
C31A	0.33453(8)	0.4379(3)	0.33562(15)	0.0296(6)	O2-	0.23544(6)	0.5893(2)	0.22398(12)	0.0367(5)
C31A-	0.16715(7)	0.7215(3)	0.31176(14)	0.0304(6)	O3	0.51641(6)	0.1764(2)	0.62730(11)	0.0427(5)
C31B	0.30025(9)	0.4017(3)	0.36727(17)	0.0368(7)	O3-	0.28608(7)	1.0071(2)	0.23512(12)	0.0441(5)
C31B-	0.14803(8)	0.6659(3)	0.36655(16)	0.0380(7)	O4	0.45562(5)	0.2292(2)	0.66342(10)	0.0328(5)
C31C	0.29377(12)	0.5051(4)	0.4199(2)	0.0591(10)	O4-	0.22570(7)	1.0568(2)	0.27387(13)	0.0500(6)
C31C-	0.17805(10)	0.6669(4)	0.44246(17)	0.0545(10)	S1	0.49480(2)	0.07197(8)	0.80745(4)	0.03569(18)
C32A	0.31773(8)	0.3454(3)	0.20911(14)	0.0341(7)	S1-	0.253046(17)	0.71051(7)	0.20912(3)	0.02572(14)
C32A-	0.12364(9)	0.8528(3)	0.20476(16)	0.0388(7)	S2	0.498272(17)	0.20785(7)	0.68310(4)	0.02766(15)
C32B	0.34083(10)	0.4110(4)	0.16265(17)	0.0445(8)	S2-	0.25619(2)	0.96542(7)	0.26864(4)	0.03059(16)

Table A-9 – Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for [$C_3(NPr_2)_3$]DCA. U(eq) is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

	x	*y*	*z*	U(eq)		*x*	*y*	*z*	U(eq)
C1	0.22573(7)	0.06754(13)	0.07272(5)	0.0231(3)	C31B	0.07648(7)	0.39678(15)	0.06347(6)	0.0317(3)
C11A	0.24199(7)	–0.03053(13)	–0.00449(5)	0.0240(3)	C31C	0.03400(8)	0.46728(16)	0.08926(7)	0.0380(4)
C11B	0.25780(7)	0.07583(14)	–0.03998(6)	0.0264(3)	C32A	0.0653(3)	0.0960(5)	–0.0226(2)	0.0263(16)
C11C	0.23230(8)	0.02684(15)	–0.09831(6)	0.0307(3)	C32A-	0.08910(10)	0.1822(2)	–0.02628(10)	0.0256(6)
C12A	0.33541(6)	–0.02442(13)	0.08798(6)	0.0246(3)	C32B	0.0770(3)	0.1966(6)	–0.0614(3)	0.0356(17)
C12B	0.34243(7)	–0.17314(14)	0.11135(6)	0.0275(3)	C32B-	0.04275(11)	0.0654(2)	–0.05862(11)	0.0332(7)
C12C	0.41422(8)	–0.20994(18)	0.14555(7)	0.0408(4)	C32C	0.0426(5)	0.1423(12)	–0.1203(4)	0.052(3)
C2	0.21393(6)	0.11453(13)	0.11651(5)	0.0223(3)	C32C-	0.02364(19)	0.0875(4)	–0.11823(15)	0.0472(9)
C21A	0.30048(7)	0.08730(16)	0.20669(6)	0.0305(3)	C4	0.17011(9)	0.76659(17)	0.13544(7)	0.0377(4)
C21B	0.35405(8)	0.19989(18)	0.22053(7)	0.0416(4)	C5	0.12489(7)	0.75638(14)	0.04446(6)	0.0285(3)
C21C	0.41954(10)	0.1462(3)	0.26250(9)	0.0678(6)	N1	0.26687(6)	0.01274(12)	0.05246(5)	0.0257(3)
C22A	0.19081(8)	0.20080(16)	0.19209(6)	0.0310(3)	N2	0.23505(6)	0.13837(12)	0.16920(4)	0.0266(3)
C22B	0.15193(9)	0.09013(18)	0.20792(7)	0.0428(4)	N3	0.10426(7)	0.16589(15)	0.03255(5)	0.0386(3)
C22C	0.10816(11)	0.1582(3)	0.23355(9)	0.0630(6)	N4	0.12249(7)	0.80173(15)	0.08955(6)	0.0427(3)
C3	0.16511(7)	0.12566(14)	0.06525(6)	0.0259(3)	N5	0.20997(10)	0.7445(2)	0.17752(7)	0.0751(6)
C31A	0.06145(7)	0.23903(15)	0.05511(6)	0.0308(3)	N6	0.12143(7)	0.72419(15)	0.00217(5)	0.0400(3)

Table A-10 – Hydrogen Atom Coordinates (Å) and Isotropic Displacement Parameters (Å^2) for [$C_3(NMe_2)_3$]TFSA.

	x	*y*	*z*	U(eq)		*x*	*y*	*z*	U(eq)
H11A	0.3407	0.4371	0.5022	0.068	H52A	–0.2884	0.8372	0.2894	0.089
H11B	0.351	0.4185	0.4209	0.068	H52B	–0.2786	0.9247	0.242	0.089
H11C	0.2786	0.4218	0.4371	0.068	H52C	–0.3374	0.8556	0.2129	0.089
H12A	0.3606	0.6409	0.3833	0.063	H61A	–0.3969	0.6483	0.2708	0.064
H12B	0.3941	0.5433	0.3822	0.063	H61B	–0.3654	0.6169	0.3524	0.064
H12C	0.4086	0.6034	0.4552	0.063	H61C	–0.3383	0.7055	0.3189	0.064
H21A	0.1823	0.4416	0.4807	0.086	H62A	–0.5025	0.7245	0.3949	0.066
H21B	0.137	0.4436	0.5403	0.086	H62B	–0.4596	0.6338	0.4096	0.066

	x	*y*	*z*	U(eq)		*x*	*y*	*z*	U(eq)
H21C	0.2147	0.4326	0.5659	0.086	H62C	–0.5066	0.6504	0.3315	0.066
H22A	0.1653	0.6696	0.588	0.067	H71A	0.0707	0.6733	0.1057	0.068
H22B	0.1434	0.5768	0.6206	0.067	H71B	0.0257	0.7037	0.0295	0.068
H22C	0.1019	0.6164	0.5454	0.067	H71C	0.0171	0.6049	0.062	0.068
H31A	0.3457	0.823	0.4914	0.07	H72A	–0.066	0.8196	0.1324	0.078
H31B	0.2945	0.8715	0.4273	0.07	H72B	–0.0161	0.8326	0.0786	0.078
H31C	0.3243	0.7745	0.4135	0.07	H72C	0.0113	0.8201	0.1645	0.078
H32A	0.1743	0.7942	0.5129	0.059	H81A	–0.105	0.7994	0.244	0.07
H32B	0.2094	0.8838	0.4913	0.059	H81B	–0.1743	0.7901	0.2675	0.07
H32C	0.2398	0.8305	0.5651	0.059	H81C	–0.1713	0.8013	0.183	0.07
H41A	–0.4508	1.0689	0.3896	0.101	H82A	–0.2339	0.6183	0.2193	0.061
H41B	–0.5238	1.0692	0.4042	0.101	H82B	–0.1968	0.6456	0.3001	0.061
H41C	–0.5118	1.0535	0.3232	0.101	H82C	–0.1737	0.5584	0.2609	0.061
H42A	–0.5687	0.8652	0.3847	0.077	H91A	–0.0035	0.4801	0.0964	0.059
H42B	–0.5614	0.9428	0.4458	0.077	H91B	–0.0508	0.3946	0.074	0.059
H42C	–0.5148	0.8555	0.4588	0.077	H91C	–0.0004	0.396	0.1512	0.059
H51A	–0.3905	1.06	0.2669	0.103	H92A	–0.0998	0.4017	0.2304	0.052
H51B	–0.3125	1.0558	0.2772	0.103	H92B	–0.1304	0.3615	0.1511	0.052
H51C	–0.3456	1.0551	0.3473	0.103	H92C	–0.1626	0.4487	0.1807	0.052

Table A-11 – Hydrogen Atom Coordinates (Å) and Isotropic Displacement Parameters (Å^2) for [$C_3(NPr_2)_3$]TFSA.

	x	*y*	*z*	U(eq)		*x*	*y*	*z*	U(eq)
H11AA	0.3562	0.1273	0.1667	0.043	H21C-B	0.1957	0.081	0.1007	0.099
H11A-A	0.0433	0.6338	0.0033	0.044	H21CC	0.4783	–0.0944	0.5843	0.077
H11AB	0.3954	0.0636	0.1557	0.043	H21C-C	0.2178	0.1729	0.0585	0.099
H11A-B	0.0637	0.7159	0.0736	0.044	H22AA	0.3775	0.3071	0.4691	0.035
H11BA	0.3308	–0.1011	0.1621	0.047	H22A-A	0.2104	0.3112	0.2924	0.038
H11B-A	0.0931	0.7125	–0.0489	0.059	H22AB	0.4088	0.2386	0.5349	0.035
H11BB	0.3658	–0.1367	0.1283	0.047	H22A-B	0.1919	0.4433	0.3119	0.038
H11B-B	0.1113	0.7997	0.0206	0.059	H22BA	0.4323	0.4008	0.4352	0.047
H11CA	0.3014	0.0387	0.0663	0.074	H22B-A	0.1564	0.1915	0.3154	0.059
H11C-A	0.0486	0.9163	–0.0037	0.117	H22BB	0.4621	0.3395	0.5054	0.047
H11CB	0.3088	–0.0976	0.0331	0.074	H22B-B	0.1393	0.3243	0.3376	0.059
H11C-B	0.0316	0.8319	–0.0744	0.117	H22CA	0.4037	0.5354	0.5052	0.093
H11CC	0.3383	0.0217	0.0348	0.074	H22C-A	0.1766	0.217	0.4423	0.121
H11C-C	0.0672	0.9323	–0.0687	0.117	H22CB	0.4307	0.4693	0.5765	0.093
H12AA	0.4241	–0.1223	0.2401	0.033	H22C-B	0.2147	0.212	0.4133	0.121
H12A-A	0.1183	0.391	0.031	0.036	H22CC	0.4507	0.5584	0.5294	0.093
H12AB	0.4399	–0.0531	0.3159	0.033	H22C-C	0.1993	0.3483	0.4343	0.121
H12A-B	0.0888	0.4685	–0.0333	0.036	H31AA	0.3283	0.5218	0.3102	0.036
H12BA	0.372	–0.2244	0.2791	0.044	H31A-A	0.1908	0.6686	0.3124	0.037
H12B-A	0.0643	0.3084	0.0661	0.053	H31AB	0.3593	0.4494	0.3749	0.036
H12BB	0.3898	–0.1591	0.3558	0.044	H31A-B	0.1763	0.8111	0.3259	0.037
H12B-B	0.0338	0.3935	0.0064	0.053	H31BA	0.2754	0.3914	0.328	0.044
H12CA	0.4141	–0.3753	0.3611	0.091	H31B-A	0.1391	0.5757	0.3533	0.046
H12C-A	0.0339	0.1757	–0.0343	0.107	H31BB	0.3063	0.3172	0.3921	0.044
H12CB	0.4311	–0.3485	0.2951	0.091	H31B-B	0.1244	0.7184	0.3665	0.046
H12C-B	0.0806	0.1842	–0.0245	0.107	H31CA	0.272	0.4778	0.4384	0.089
H12CC	0.4509	–0.2788	0.3698	0.091	H31CB	0.2871	0.5885	0.3953	0.089
H12C-C	0.0503	0.2695	–0.0843	0.107	H31CC	0.3181	0.5145	0.4594	0.089

	x	*y*	*z*	U(eq)		*x*	*y*	*z*	U(eq)
H1C-A	0.2009	0.6123	0.443	0.082	H32AA	0.293	0.395	0.205	0.041
H1C-B	0.1651	0.633	0.4767	0.082	H32A-A	0.1083	0.8387	0.1545	0.047
H1C-C	0.187	0.7561	0.4554	0.082	H32AB	0.3101	0.2566	0.191	0.041
H21AA	0.4417	0.0017	0.4324	0.033	H32A-B	0.1462	0.9109	0.2054	0.047
H21A-A	0.136	0.2578	0.1283	0.039	H32BA	0.3462	0.5027	0.1775	0.053
H21AB	0.4611	0.0936	0.4991	0.033	H32B-A	0.0767	0.8574	0.2495	0.057
H21A-B	0.1653	0.1783	0.1922	0.039	H32BB	0.3666	0.3665	0.1698	0.053
H21BA	0.3982	–0.0893	0.4921	0.045	H32B-B	0.1131	0.948	0.2911	0.057
H21B-A	0.2215	0.2761	0.1676	0.05	H32CA	0.2907	0.4434	0.0759	0.101
H21BB	0.415	0.0076	0.5578	0.045	H32C-A	0.0576	1.0113	0.1553	0.098
H21B-B	0.1927	0.3608	0.1053	0.05	H32CB	0.3145	0.3156	0.0663	0.101
H21CA	0.4625	–0.1887	0.5173	0.077	H32C-B	0.0605	1.0853	0.2283	0.098
H21C-A	0.1704	0.1706	0.0372	0.099	H32CC	0.3312	0.456	0.0549	0.101
H21CB	0.4453	–0.2016	0.5841	0.077	H32C-C	0.0955	1.0992	0.1918	0.098

Table A-12 – Hydrogen Atom Coordinates (Å) and Isotropic Displacement Parameters (Å^2) for [$C_3(NPr_2)_3$]DCA.

	x	*y*	*z*	U(eq)		*x*	*y*	*z*	U(eq)
H11AA	0.1941	–0.043	–0.0181	0.029	H22CA	0.0767	0.221	0.208	0.095
H11AB	0.2615	–0.1214	–0.0069	0.029	H22CB	0.0847	0.0854	0.2437	0.095
H11BA	0.2377	0.1664	–0.0383	0.032	H22CC	0.1356	0.2109	0.265	0.095
H11BB	0.3056	0.0894	–0.0263	0.032	H31AA	0.0677	0.196	0.0894	0.037
H11CA	0.2425	0.0973	–0.1196	0.046	H31AB	0.0152	0.2263	0.0309	0.037
H11CB	0.2534	–0.0612	–0.1003	0.046	H31BA	0.0679	0.4413	0.029	0.038
H11CC	0.1849	0.0134	–0.112	0.046	H31BB	0.1232	0.4101	0.0864	0.038
H12AA	0.3633	–0.0164	0.0678	0.029	H31CA	–0.0122	0.4509	0.0673	0.057
H12AB	0.3516	0.0433	0.1174	0.029	H31CB	0.0448	0.428	0.1246	0.057
H12BA	0.3165	–0.1802	0.1332	0.033	H31CC	0.0426	0.5675	0.0922	0.057
H12BB	0.3246	–0.2411	0.0821	0.033	H32AA	0.0183	0.0887	–0.0299	0.032
H12CA	0.4321	–0.1427	0.1745	0.061	H32A-A	0.1302	0.1786	–0.0319	0.031
H12CB	0.4165	–0.3035	0.1602	0.061	H32AB	0.0826	0.0021	–0.0244	0.032
H12CC	0.4397	–0.207	0.1237	0.061	H32A-B	0.0685	0.2738	–0.0387	0.031
H21AA	0.3133	0.0066	0.1907	0.037	H32BA	0.0595	0.2895	–0.0586	0.043
H21AB	0.2971	0.0552	0.2397	0.037	H32B-A	0.003	0.0649	–0.0511	0.04
H21BA	0.3602	0.2269	0.1881	0.05	H32BB	0.1245	0.2061	–0.0518	0.043
H21BB	0.3401	0.2835	0.2343	0.05	H32B-B	0.0646	–0.0258	–0.0479	0.04
H21CA	0.4335	0.0639	0.2488	0.102	H32CA	–0.0046	0.1372	–0.1304	0.078
H21CB	0.4138	0.1217	0.2949	0.102	H32C-A	–0.0018	0.0076	–0.1378	0.071
H21CC	0.4527	0.2191	0.2703	0.102	H32CB	0.0594	0.0497	–0.123	0.078
H22AA	0.1599	0.2646	0.1658	0.037	H32C-B	–0.0026	0.1722	–0.1296	0.071
H22AB	0.2171	0.2562	0.2237	0.037	H32CC	0.0519	0.2064	–0.1441	0.078
H22BA	0.1241	0.037	0.1762	0.051	H32C-C	0.0632	0.0966	–0.1252	0.071
H22BB	0.1827	0.0242	0.2333	0.051					

Table A-13 – Anisotropic Displacement Parameters (Å^2) for [$C_3(NMe_2)_3$]TFSA. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka\times b\times U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0306(14)	0.0256(13)	0.0231(12)	0.0001(11)	0.0009(11)	–0.0033(11)
C10	0.0406(17)	0.0499(19)	0.0316(15)	–0.0017(14)	0.0115(13)	–0.0063(14)
C11	0.057(2)	0.0312(16)	0.0484(17)	–0.0069(14)	0.0129(15)	0.0043(14)
C12	0.0441(17)	0.0480(18)	0.0368(15)	–0.0012(14)	0.0174(13)	0.0010(14)
C2	0.0302(14)	0.0288(14)	0.0243(12)	0.0030(11)	0.0030(11)	–0.0005(11)
C20	0.0368(16)	0.0348(16)	0.0451(16)	–0.0057(14)	0.0130(13)	–0.0020(13)
C21	0.069(2)	0.0366(18)	0.075(2)	0.0126(17)	0.0349(19)	–0.0090(16)
C22	0.0452(18)	0.054(2)	0.0387(16)	0.0118(15)	0.0167(14)	0.0060(15)
C3	0.0300(14)	0.0280(14)	0.0216(12)	0.0004(11)	0.0024(10)	–0.0023(11)
C30	0.0312(15)	0.0391(17)	0.0477(17)	–0.0060(14)	0.0109(13)	–0.0001(13)
C31	0.0530(19)	0.0296(16)	0.063(2)	–0.0029(14)	0.0227(16)	–0.0117(14)
C32	0.0464(17)	0.0303(15)	0.0414(16)	–0.0003(13)	0.0090(13)	0.0077(13)
C4	0.0234(13)	0.0266(14)	0.0410(15)	–0.0044(12)	–0.0026(12)	–0.0032(11)
C40	0.0432(17)	0.0418(18)	0.0415(16)	0.0003(14)	0.0125(14)	–0.0083(14)
C41	0.095(3)	0.0370(19)	0.063(2)	–0.0130(17)	0.001(2)	0.0255(19)
C42	0.0402(18)	0.073(2)	0.0425(17)	–0.0083(16)	0.0120(14)	0.0148(16)
C5	0.0245(14)	0.0318(15)	0.0403(15)	0.0083(12)	–0.0020(12)	–0.0036(11)
C50	0.0430(17)	0.0490(19)	0.0338(15)	0.0059(14)	0.0149(13)	–0.0088(14)
C51	0.071(2)	0.052(2)	0.077(2)	0.0245(19)	0.001(2)	–0.0303(19)
C52	0.0393(18)	0.095(3)	0.0451(18)	0.0155(19)	0.0123(15)	–0.0133(18)
C6	0.0243(13)	0.0268(14)	0.0347(14)	–0.0006(11)	0.0055(11)	–0.0012(10)
C60	0.0322(15)	0.0434(17)	0.0354(15)	–0.0039(13)	0.0118(12)	0.0014(13)
C61	0.0432(17)	0.0335(16)	0.0532(18)	–0.0021(14)	0.0128(14)	0.0103(13)
C62	0.0459(18)	0.0270(16)	0.0609(19)	0.0003(14)	0.0168(15)	–0.0086(13)
C7	0.0308(14)	0.0232(13)	0.0202(12)	0.0016(10)	0.0042(10)	–0.0018(10)
C71	0.0447(18)	0.056(2)	0.0392(16)	0.0063(15)	0.0200(14)	–0.0102(15)
C72	0.065(2)	0.0302(17)	0.062(2)	0.0068(15)	0.0185(17)	–0.0136(15)
C8	0.0296(13)	0.0230(13)	0.0217(12)	0.0002(10)	0.0049(11)	0.0013(10)
C81	0.0546(19)	0.0319(16)	0.0561(19)	–0.0140(14)	0.0191(16)	0.0058(14)
C82	0.0431(17)	0.0471(18)	0.0365(15)	–0.0057(13)	0.0213(13)	0.0007(14)
C9	0.0262(13)	0.0258(14)	0.0201(11)	0.0007(10)	0.0062(10)	0.0002(10)
C91	0.0401(16)	0.0323(16)	0.0498(17)	–0.0102(13)	0.0194(14)	0.0004(12)
C92	0.0423(16)	0.0230(14)	0.0424(15)	0.0024(12)	0.0183(13)	–0.0042(12)
F11	0.0468(11)	0.0897(15)	0.0768(13)	–0.0041(12)	0.0327(10)	–0.0043(11)
F12	0.0780(13)	0.0643(13)	0.0389(10)	0.0139(9)	0.0107(9)	–0.0213(10)
F13	0.0636(12)	0.0579(12)	0.0464(10)	–0.0130(9)	0.0180(9)	–0.0296(9)
F21	0.0544(12)	0.0737(14)	0.0676(12)	–0.0084(11)	0.0104(10)	–0.0364(10)
F22	0.0596(12)	0.0620(12)	0.0604(11)	–0.0095(10)	0.0360(10)	–0.0036(9)
F23	0.0643(12)	0.0358(10)	0.0642(11)	0.0137(9)	0.0274(9)	0.0017(8)
F31	0.0383(10)	0.0663(13)	0.0981(15)	–0.0183(11)	0.0320(10)	–0.0035(9)
F32	0.0685(13)	0.0610(13)	0.0602(12)	0.0184(10)	0.0130(10)	–0.0155(10)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F33	0.0462(10)	0.0473(11)	0.0682(12)	–0.0217(9)	0.0171(9)	–0.0137(8)
F41	0.0714(14)	0.0879(16)	0.0630(12)	–0.0061(11)	0.0430(11)	–0.0187(11)
F42	0.0612(12)	0.0671(13)	0.0649(12)	–0.0021(10)	0.0066(10)	–0.0373(10)
F43	0.0721(13)	0.0497(12)	0.0732(13)	0.0273(10)	0.0127(11)	–0.0074(10)
F51	0.0516(12)	0.0897(16)	0.0905(15)	0.0002(13)	0.0454(11)	–0.0099(11)
F52	0.0809(14)	0.0713(14)	0.0413(10)	0.0240(10)	0.0093(9)	–0.0306(11)
F53	0.0605(11)	0.0518(11)	0.0467(10)	0.0030(9)	0.0075(9)	–0.0303(9)
F61	0.0406(10)	0.0838(14)	0.0554(11)	0.0048(10)	0.0045(9)	–0.0237(10)
F62	0.0588(12)	0.0721(13)	0.0494(10)	–0.0030(9)	0.0334(9)	0.0069(10)
F63	0.0530(11)	0.0363(10)	0.0616(11)	0.0089(8)	0.0303(9)	0.0014(8)
N10	0.0352(12)	0.0267(12)	0.0337(12)	–0.0017(10)	0.0071(10)	0.0004(10)
N2	0.0291(12)	0.0286(12)	0.0269(11)	–0.0026(9)	–0.0009(9)	0.0019(9)
N20	0.0426(14)	0.0304(13)	0.0396(13)	0.0097(10)	0.0180(11)	–0.0012(10)
N30	0.0414(13)	0.0206(12)	0.0333(12)	–0.0011(9)	0.0121(10)	–0.0033(9)
N4	0.0270(11)	0.0305(12)	0.0255(11)	–0.0012(9)	0.0020(9)	0.0023(9)
N40	0.0297(13)	0.0323(13)	0.0627(16)	–0.0144(12)	0.0018(12)	0.0053(10)
N5	0.0291(12)	0.0319(12)	0.0246(10)	0.0036(9)	0.0013(9)	0.0006(9)
N50	0.0282(13)	0.0453(15)	0.0598(16)	0.0221(13)	0.0018(12)	–0.0078(11)
N60	0.0362(13)	0.0234(12)	0.0535(15)	–0.0031(11)	0.0179(11)	–0.0004(10)
N70	0.0426(13)	0.0279(12)	0.0339(12)	0.0046(10)	0.0142(10)	–0.0076(10)
N80	0.0392(13)	0.0265(12)	0.0348(12)	–0.0045(10)	0.0162(10)	0.0029(10)
N90	0.0327(12)	0.0181(11)	0.0427(13)	–0.0001(9)	0.0186(10)	0.0008(9)
O11	0.0517(12)	0.0355(11)	0.0364(10)	–0.0100(9)	0.0113(9)	0.0035(9)
O12	0.0374(11)	0.0399(11)	0.0317(10)	0.0037(8)	0.0032(8)	0.0093(9)
O21	0.0410(11)	0.0301(11)	0.0534(12)	–0.0052(9)	0.0025(9)	0.0121(8)
O22	0.0353(10)	0.0298(10)	0.0337(10)	–0.0073(8)	0.0045(8)	–0.0048(8)
O31	0.0454(12)	0.0367(11)	0.0469(11)	–0.0136(9)	0.0119(9)	0.0033(9)
O32	0.0451(12)	0.0448(12)	0.0423(11)	0.0052(10)	–0.0018(9)	0.0155(10)
O41	0.0384(11)	0.0375(11)	0.0329(10)	–0.0094(8)	0.0043(8)	–0.0052(8)
O42	0.0370(11)	0.0342(11)	0.0507(12)	–0.0039(9)	0.0055(9)	0.0103(9)
O51	0.0578(13)	0.0339(11)	0.0288(10)	–0.0069(8)	0.0125(9)	–0.0020(9)
O52	0.0360(10)	0.0286(10)	0.0303(9)	0.0056(8)	0.0079(8)	0.0028(8)
O61	0.0405(11)	0.0447(12)	0.0371(10)	–0.0150(9)	0.0052(9)	–0.0056(9)
O62	0.0507(13)	0.0324(11)	0.0680(14)	0.0002(10)	0.0130(11)	0.0160(9)
S1	0.0322(3)	0.0277(3)	0.0257(3)	–0.0018(3)	0.0058(3)	0.0021(3)
S2	0.0293(3)	0.0213(3)	0.0322(3)	–0.0033(3)	0.0039(3)	0.0004(3)
S3	0.0305(4)	0.0272(3)	0.0330(3)	–0.0021(3)	0.0044(3)	0.0050(3)
S4	0.0285(3)	0.0242(3)	0.0293(3)	–0.0025(3)	0.0055(3)	–0.0010(3)
S5	0.0328(4)	0.0240(3)	0.0244(3)	0.0005(3)	0.0093(3)	–0.0026(3)
S6	0.0317(4)	0.0260(3)	0.0354(4)	–0.0041(3)	0.0075(3)	0.0025(3)

Table A-14 – Anisotropic Displacement Parameters (Å^2) for [$C_3(NPr_2)_3$]TFSA. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka\times b\times U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0216(12)	0.0280(14)	0.0245(14)	0.0011(12)	0.0034(10)	–0.0004(11)
C1-	0.0248(12)	0.0304(14)	0.0238(14)	0.0019(12)	0.0077(10)	0.0028(11)
C11A	0.0460(16)	0.0343(16)	0.0250(15)	0.0008(13)	0.0084(12)	0.0052(13)
C11A-	0.0392(15)	0.0389(17)	0.0285(15)	0.0044(13)	0.0049(12)	0.0102(13)
C11B	0.0382(15)	0.048(2)	0.0308(16)	–0.0012(15)	0.0094(12)	–0.0041(14)
C11B-	0.068(2)	0.0369(18)	0.042(2)	0.0019(16)	0.0169(16)	0.0034(16)
C11C	0.0460(17)	0.070(2)	0.0310(17)	–0.0055(18)	0.0095(13)	0.0015(17)
C11C-	0.127(4)	0.036(2)	0.057(3)	0.011(2)	0.003(2)	0.015(2)
C12A	0.0247(12)	0.0284(14)	0.0297(15)	–0.0017(12)	0.0070(11)	0.0048(11)
C12A-	0.0299(13)	0.0332(16)	0.0236(14)	–0.0045(12)	0.0041(11)	0.0041(12)
C12B	0.0289(14)	0.0313(16)	0.0474(19)	0.0038(14)	0.0060(12)	–0.0026(12)
C12B-	0.0412(16)	0.0417(19)	0.0470(19)	0.0045(16)	0.0088(14)	0.0033(15)
C12C	0.059(2)	0.034(2)	0.080(3)	0.018(2)	0.0049(19)	0.0051(16)
C12C-	0.073(2)	0.046(2)	0.079(3)	–0.010(2)	–0.004(2)	–0.012(2)
C2	0.0193(11)	0.0257(13)	0.0244(13)	0.0018(11)	0.0067(10)	0.0002(10)
C2-	0.0212(11)	0.0295(15)	0.0205(13)	0.0024(12)	0.0057(10)	–0.0011(11)
C21A	0.0272(13)	0.0304(15)	0.0228(13)	0.0032(12)	0.0040(10)	0.0056(11)
C21A-	0.0336(14)	0.0258(14)	0.0321(15)	0.0000(12)	0.0011(11)	0.0027(12)
C21B	0.0514(17)	0.0300(16)	0.0300(15)	0.0039(14)	0.0089(13)	–0.0024(14)
C21B-	0.0422(16)	0.0422(18)	0.0392(18)	–0.0013(15)	0.0102(13)	0.0098(14)
C21C	0.082(2)	0.0336(18)	0.0374(19)	0.0105(16)	0.0149(17)	0.0120(17)
C21C-	0.089(3)	0.060(2)	0.052(2)	–0.007(2)	0.024(2)	0.025(2)
C22A	0.0335(13)	0.0309(15)	0.0208(14)	0.0012(12)	0.0057(11)	0.0063(12)
C22A-	0.0307(13)	0.0301(15)	0.0264(14)	0.0051(13)	–0.0034(11)	0.0015(12)
C22B	0.0412(16)	0.0320(16)	0.0389(17)	0.0034(14)	0.0015(13)	–0.0016(13)
C22B-	0.061(2)	0.051(2)	0.0359(19)	0.0114(16)	0.0127(15)	–0.0046(17)
C22C	0.074(2)	0.0355(19)	0.060(2)	–0.0076(18)	–0.006(2)	0.0033(18)
C22C-	0.125(4)	0.074(3)	0.034(2)	0.022(2)	0.008(2)	–0.001(3)
C3	0.0221(11)	0.0282(15)	0.0246(13)	0.0003(12)	0.0053(10)	–0.0020(11)
C3-	0.0262(12)	0.0291(15)	0.0221(14)	0.0025(11)	0.0076(10)	0.0035(11)
C31A	0.0294(13)	0.0273(15)	0.0283(14)	0.0006(12)	0.0022(11)	0.0029(11)
C31A-	0.0283(12)	0.0348(15)	0.0265(14)	–0.0054(13)	0.0053(10)	0.0017(12)
C31B	0.0330(14)	0.0380(17)	0.0398(17)	0.0000(14)	0.0113(13)	0.0047(13)
C31B-	0.0310(14)	0.0500(19)	0.0354(16)	0.0035(15)	0.0134(12)	0.0064(13)
C31C	0.069(2)	0.055(2)	0.060(2)	–0.002(2)	0.031(2)	0.0187(19)
C31C-	0.0492(18)	0.086(3)	0.0279(17)	0.0042(18)	0.0103(14)	0.0181(19)
C32A	0.0352(14)	0.0347(16)	0.0258(14)	0.0010(13)	–0.0016(11)	0.0081(13)
C32A-	0.0469(17)	0.0323(16)	0.0350(17)	–0.0011(14)	0.0083(13)	0.0019(14)
C32B	0.0551(19)	0.0443(19)	0.0332(17)	0.0082(15)	0.0114(14)	0.0094(16)
C32B-	0.0433(17)	0.0294(16)	0.075(3)	0.0011(17)	0.0268(17)	0.0021(14)
C32C	0.096(3)	0.073(3)	0.0307(19)	0.0117(19)	0.0143(19)	0.033(2)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C32C-	0.051(2)	0.035(2)	0.111(4)	0.008(2)	0.026(2)	0.0077(16)
C4	0.0381(15)	0.0456(19)	0.0345(17)	0.0029(15)	0.0129(13)	–0.0018(14)
C4-	0.0357(15)	0.0431(19)	0.0292(15)	–0.0050(14)	0.0056(12)	0.0031(13)
C5	0.0307(14)	0.0400(18)	0.0427(18)	–0.0025(16)	0.0036(13)	–0.0021(13)
C5-	0.0387(15)	0.0377(18)	0.0342(17)	–0.0067(14)	0.0039(13)	–0.0024(14)
F1	0.0594(11)	0.0393(11)	0.0731(14)	–0.0081(11)	0.0265(10)	–0.0005(9)
F1-	0.0588(11)	0.0540(12)	0.0304(9)	0.0131(9)	0.0085(8)	–0.0027(9)
F2	0.0479(10)	0.0650(14)	0.0454(11)	0.0018(11)	–0.0035(8)	–0.0164(10)
F2-	0.0319(8)	0.0923(17)	0.0370(10)	0.0051(11)	–0.0054(7)	–0.0049(10)
F3	0.0849(15)	0.0632(14)	0.0655(14)	0.0128(12)	0.0454(12)	–0.0093(12)
F3-	0.0810(14)	0.0655(14)	0.0360(11)	–0.0180(11)	0.0106(10)	0.0152(12)
F4	0.0279(8)	0.0587(13)	0.0857(15)	–0.0127(12)	0.0037(9)	–0.0109(9)
F4-	0.0448(10)	0.0711(14)	0.0455(11)	0.0008(11)	–0.0078(8)	0.0171(10)
F5	0.0642(12)	0.0483(12)	0.0629(14)	–0.0229(11)	0.0198(10)	–0.0041(10)
F5-	0.0622(12)	0.0820(16)	0.0312(10)	0.0037(11)	0.0151(9)	–0.0043(11)
F6	0.0605(12)	0.0439(12)	0.0789(15)	0.0180(12)	0.0000(11)	–0.0126(10)
F6-	0.0867(15)	0.0630(14)	0.0507(13)	–0.0208(12)	0.0031(11)	–0.0262(13)
N1	0.0337(12)	0.0275(12)	0.0235(12)	0.0010(10)	0.0052(9)	0.0071(10)
N1-	0.0330(12)	0.0320(13)	0.0213(11)	–0.0007(11)	–0.0006(9)	0.0097(10)
N2	0.0253(10)	0.0279(12)	0.0219(11)	0.0046(10)	0.0041(9)	0.0039(9)
N2-	0.0261(10)	0.0283(12)	0.0240(11)	0.0057(10)	0.0010(9)	0.0045(9)
N3	0.0303(11)	0.0281(12)	0.0242(12)	0.0015(10)	0.0005(9)	0.0076(10)
N3-	0.0364(12)	0.0300(13)	0.0258(12)	–0.0022(11)	0.0041(9)	0.0041(11)
N4	0.0261(11)	0.0366(14)	0.0315(13)	–0.0002(11)	0.0055(10)	0.0041(10)
N4-	0.0256(11)	0.0309(13)	0.0294(12)	–0.0021(11)	0.0062(9)	0.0003(10)
O1	0.0702(15)	0.0599(17)	0.0303(12)	0.0101(12)	–0.0138(11)	–0.0016(13)
O1-	0.0222(8)	0.0346(10)	0.0384(11)	0.0009(10)	0.0057(7)	0.0032(9)
O2	0.0690(15)	0.0565(15)	0.0398(13)	–0.0007(12)	0.0321(11)	0.0137(12)
O2-	0.0394(11)	0.0273(11)	0.0419(12)	0.0017(10)	0.0093(9)	–0.0048(9)
O3	0.0447(11)	0.0532(15)	0.0361(12)	–0.0039(11)	0.0212(9)	–0.0027(10)
O3-	0.0572(13)	0.0348(12)	0.0454(13)	0.0012(10)	0.0227(11)	–0.0113(10)
O4	0.0224(8)	0.0417(12)	0.0311(10)	0.0053(10)	0.0025(7)	0.0012(8)
O4-	0.0603(14)	0.0388(13)	0.0480(14)	–0.0011(12)	0.0108(11)	0.0220(11)
S1	0.0424(4)	0.0407(4)	0.0211(3)	0.0002(3)	0.0045(3)	0.0025(3)
S1-	0.0240(3)	0.0256(3)	0.0258(3)	0.0008(3)	0.0043(2)	0.0004(3)
S2	0.0231(3)	0.0339(4)	0.0256(3)	–0.0022(3)	0.0065(2)	–0.0003(3)
S2-	0.0372(3)	0.0243(3)	0.0288(4)	0.0013(3)	0.0071(3)	0.0035(3)

Table A-15 – Anisotropic Displacement Parameters ($Å^2$) for $[C_3(NPr_2)_3]DCA$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka\times b\times U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0292(7)	0.0189(6)	0.0223(7)	0.0028(5)	0.0116(6)	0.0010(5)
C11A	0.0287(7)	0.0211(6)	0.0249(7)	–0.0027(5)	0.0136(6)	–0.0010(5)
C11B	0.0314(7)	0.0216(6)	0.0301(7)	–0.0015(5)	0.0164(6)	–0.0027(5)
C11C	0.0391(8)	0.0276(7)	0.0285(8)	0.0011(6)	0.0167(7)	–0.0031(6)
C12A	0.0241(7)	0.0236(6)	0.0277(7)	–0.0018(5)	0.0121(6)	–0.0014(5)
C12B	0.0319(8)	0.0246(6)	0.0297(7)	0.0013(5)	0.0161(6)	0.0005(5)
C12C	0.0372(9)	0.0458(9)	0.0433(9)	0.0147(7)	0.0203(8)	0.0116(7)
C2	0.0264(7)	0.0193(6)	0.0239(7)	0.0023(5)	0.0128(6)	0.0002(5)
C21A	0.0306(8)	0.0353(8)	0.0230(7)	0.0003(6)	0.0078(6)	0.0026(6)
C21B	0.0395(9)	0.0467(9)	0.0380(9)	–0.0119(7)	0.0149(8)	–0.0063(7)
C21C	0.0390(11)	0.0962(17)	0.0540(13)	–0.0192(11)	0.0035(10)	–0.0083(11)
C22A	0.0358(8)	0.0346(7)	0.0248(7)	–0.0014(6)	0.0145(6)	0.0058(6)
C22B	0.0468(10)	0.0491(9)	0.0425(10)	–0.0007(8)	0.0282(8)	–0.0007(8)
C22C	0.0627(13)	0.0886(15)	0.0562(13)	–0.0145(11)	0.0431(11)	–0.0074(11)
C3	0.0295(7)	0.0250(6)	0.0242(7)	0.0015(5)	0.0116(6)	0.0050(5)
C31A	0.0266(7)	0.0333(7)	0.0333(8)	0.0020(6)	0.0128(6)	0.0073(6)
C31B	0.0292(7)	0.0338(7)	0.0365(8)	0.0069(6)	0.0177(7)	0.0047(6)
C31C	0.0377(9)	0.0354(8)	0.0462(10)	–0.0014(7)	0.0224(8)	0.0034(7)
C32A	0.020(3)	0.023(3)	0.030(4)	–0.002(2)	0.004(2)	0.000(2)
C32A-	0.0281(11)	0.0219(10)	0.0248(14)	0.0040(8)	0.0084(9)	0.0021(8)
C32B	0.030(3)	0.043(3)	0.031(4)	0.007(3)	0.010(3)	0.007(2)
C32B-	0.0246(11)	0.0325(11)	0.0358(16)	–0.0060(10)	0.0048(11)	0.0014(8)
C32C	0.040(5)	0.089(8)	0.023(3)	0.010(4)	0.009(3)	0.000(4)
C32C-	0.040(2)	0.061(2)	0.0339(15)	–0.0096(15)	0.0084(14)	0.0090(14)
C4	0.0436(10)	0.0402(8)	0.0356(9)	–0.0017(7)	0.0223(8)	0.0039(7)
C5	0.0229(7)	0.0281(7)	0.0338(8)	0.0069(6)	0.0104(6)	0.0024(5)
N1	0.0267(6)	0.0273(6)	0.0239(6)	–0.0019(4)	0.0111(5)	0.0036(4)
N2	0.0287(6)	0.0319(6)	0.0196(6)	0.0001(5)	0.0100(5)	0.0033(5)
N3	0.0337(7)	0.0512(8)	0.0250(7)	–0.0009(6)	0.0053(6)	0.0197(6)
N4	0.0420(8)	0.0500(8)	0.0382(8)	0.0002(6)	0.0184(7)	0.0143(6)
N5	0.0791(13)	0.1111(16)	0.0307(9)	–0.0020(9)	0.0174(9)	0.0315(12)
N6	0.0366(8)	0.0487(8)	0.0323(8)	0.0061(6)	0.0112(6)	0.0064(6)